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XLIX. *On the Cathode Dark Space in the Geissler Discharge.* By E. C. CHILDS, B.Sc.*

SERIOUS investigation of the cathode (or Crookes's) dark space in the Geissler discharge seems first to have been begun by Aston ⁽¹⁾ in 1911. As is well known, when a current of electricity is passed between metal electrodes in gases at low pressure, we have, going from the anode to the cathode, the positive glow or column, the Faraday dark space, the negative glow, the Crookes's dark space, and, in a few gases, a very thin region next to the cathode known as the primary dark space. As the pressure of gas decreases, these glows and dark spaces move towards the anode, and at pressures of the order of a millimetre of mercury the positive column and Faraday dark space disappear. It was this type of discharge that was studied by Aston. It was pointed out that for reasons which differ from those commonly accepted nowadays, the distribution of potential and electric field in the region of the cathode dark space cannot be ascertained with any degree of reliability by any method which depends on the introduction of a probe into the discharge. In consequence, a method was devised in which a stream of cathode rays, generated in a side tube, was projected across the main

* Communicated by Prof. E. V. Appleton, F.R.S.

tube, the deflexion of the spot on a willemite screen being a measure of the electric intensity at right angles to the path of the beam (*i. e.* along the main tube). The conclusion drawn from the results of this experiment was that in such a discharge the fall of potential along the tube is entirely localized in the cathode dark space, the negative glow being wholly at anode potential.

This work led to perhaps a more important investigation ⁽²⁾ of the relations holding between the current density, the potential difference across the cathode dark space (and incidentally across the tube), the length of the dark space, and the pressure of gas in a discharge-tube, using various active and inert gases. It was found that the active gases obeyed, to a fair degree of accuracy, the empirical equations :

$$D = A/P + B/C^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$V = E + FC^{\frac{1}{2}}/P, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which A, B, E, and F are constants. Throughout this paper the length of the cathode dark space will be represented by D, the potential difference between the electrodes by V, the current density by C, and the pressure of gas in the tube by P.

The behaviour of the inert gases deviated slightly from that of the active gases, and it was found that they obeyed more closely an equation derived by eliminating P between (1) and (2), *i. e.*

$$V - G = KDC^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

G and K being constants containing A, B, E, and F. These experiments were conducted with a discharge-tube containing a cathode surrounded by a guard-ring, but it was assumed that the current density was uniform over a large proportion of the total area. It will be shown in this paper that this assumption is not valid.

In the light of modern work on space-charge and the current across ionic sheaths, the cathode dark space assumes a new significance. Langmuir ⁽³⁾ has shown, both theoretically and practically, that a probe introduced into a gas discharge becomes surrounded by a sheath of electrons or positive ions, according to whether the probe is at a positive or negative potential respectively with respect to the space potential. The potential difference between the probe and the region of the discharge into which it is

introduced is localized in this sheath, which is a property, as we have seen, of the cathode dark space. An attempt has been made by Ryde to show that the dark space in the Geissler discharge is in effect a sheath of positive ions whose space-charge limits the current passing through the tube.

If we have a plane source emitting a copious supply of current carriers with zero velocity, and they are accelerated by a potential v to a plane parallel collector separated from the emitter by a distance d , the resulting current will be of the form ⁽⁴⁾:

$$C = Lv^{\frac{3}{2}}/d^2, \dots \dots \dots (4)$$

where L is a constant involving the charge and mass of the carrier. Assuming with Ryde ⁽⁵⁾ that the above case and that of the cathode dark space are identical (*i. e.* the boundary of the negative glow is the emitter, and the cathode the collector of positive ions), we are at once in disagreement with Aston's experimental results.

It was thought that the discrepancy might be more apparent than real, the cause being partly the inefficiency of Aston's guard-ring and partly the fact that the potential difference across the tube may not coincide with that across the cathode dark space. Emeléus and Harris ⁽⁶⁾ have found that the potential of the negative glow boundary of the dark space may be either negative or positive with respect to the anode. The present experiments were conceived with the idea of eliminating these causes of uncertainty, and deciding which, if either, of the rival laws is true.

A preliminary series of experiments was carried out in order to find the relative sizes of cathode and guard-ring for the latter to be efficient. A discharge-tube was constructed having an ordinary plane disk anode of duralumin, 9.8 cm. in diameter, but the cathode was peculiar in that it consisted of a small disk surrounded by four concentric rings, all of duralumin. The dimensions of this "split" cathode are given in Table I.

The rings were mounted on a brass plate, from which they were insulated by a disk of mica. Small lengths of brass rod were screwed into the underside of the rings and passed through the brass plate, from which they were insulated by glass tube. Another disk of mica was placed over the protruding ends, and brass nuts on the screwed

rods served to clamp the rings to the plate. The under-side of the plate was well waxed to render the assembly air-tight, the leads to the split cathode being soldered to the ends of the rods.

A glass bell-jar was ground onto the base-plate and waxed down, provision for the anode rod and pumping being made at the top by means of a brass cap fitted with two tubes. This tube was constructed by Mr. N. L. Harris, now of the General Electric Company. When it was in use the air was first pumped out by a Cenco Hyvac pump, and then hydrogen was admitted from a coal-gas flame by means of a palladium tube, the gas-pressure being measured by a McLeod gauge, a liquid-air

TABLE I.

| Ring. | Inner diameter. | Outer diameter. | Area. |
|---------|-----------------|-----------------|---------------|
| 1 | 0 cm. | 2.315 cm. | 4.20 sq. cm. |
| 2 | 2.355 cm. | 4.115 cm. | 8.95 sq. cm. |
| 3 | 4.215 cm. | 6.075 cm. | 15.04 sq. cm. |
| 4 | 6.150 cm. | 7.940 cm. | 19.80 sq. cm. |
| 5 | 8.000 cm. | 9.740 cm. | 24.25 sq. cm. |

trap ensuring that no mercury vapour passed into the experimental tube.

The electrical connexions are shown in fig. 1, in which A is a milliammeter indicating the total current through the tube produced by the battery B_1 and regulated by the saturated diode D. The tube voltage is indicated by the voltmeter V. Each of the cathode rings C is connected to one of a system of mercury cups M, provided with interchangeable links, in one of which is a galvanometer a and potential divider P fed from a second battery of lead accumulators B_2 .

It will at once be apparent from this that not only can the current to any one ring be measured, but also the potential of any ring with respect to the others can be varied at will.

With this tube the current densities at five different distances from the centre of the cathode were measured. The mean current density over a ring was taken to be the

same as that at a distance from the centre equal to the arithmetic mean of the inner and outer radii. It was found that at the lower pressures, *i. e.* pressures less than about .8 mm. of mercury, the current density was reasonably uniform over all but the outermost of the five rings, but at higher pressures considerably more current passed to the outer rings than to the inner. Such a case is shown in fig. 2, drawn from the data in Table II.

Fig. 1.

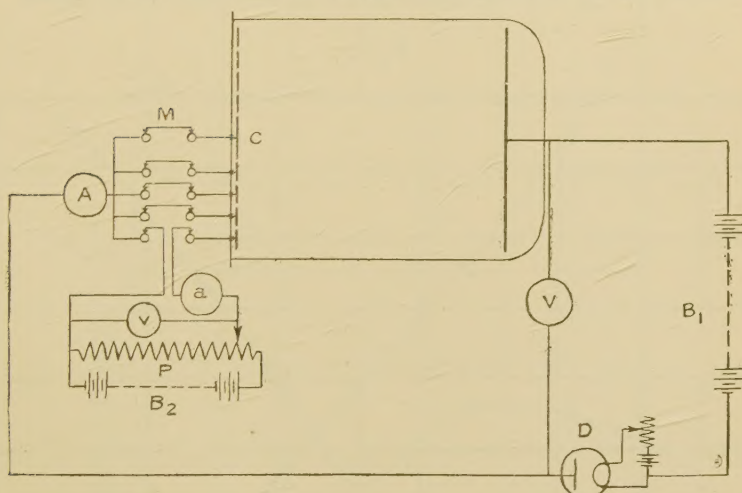


TABLE II.

Gas-pressure = 1.24 mm. Hg.

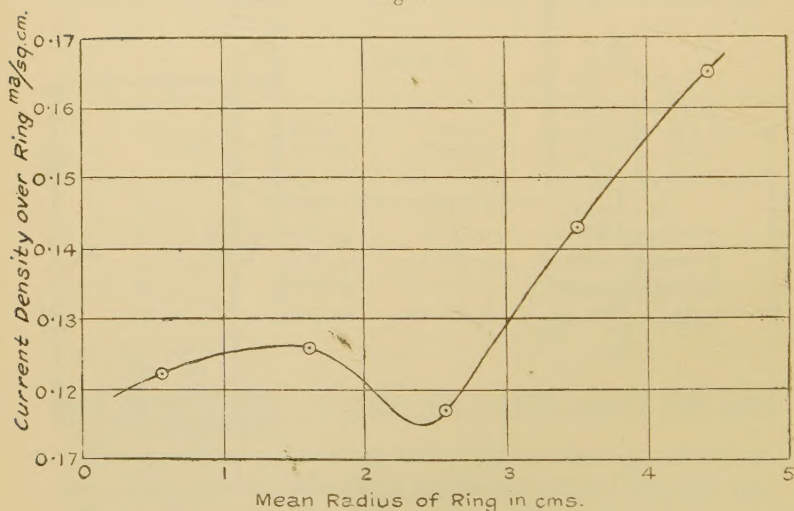
Tube voltage = 240.

Tube current = 10 m.a.

| Ring. | Mean distance from centre. | Current density. |
|---------|-------------------------------|--------------------|
| 1 | 0.58 cm. | 0.122 m.a./sq. cm. |
| 2 | 1.62 cm. | 0.126 m.a./sq. cm. |
| 3 | 2.57 cm. | 0.117 m.a./sq. cm. |
| 4 | 3.52 cm. | 0.143 m.a./sq. cm. |
| 5 | 4.44 cm. | 0.165 m.a./sq. cm. |

It must be understood that only those cases have been considered in which the tube current is sufficiently large for the glow to cover the cathode, a condition which has been called the abnormal cathode fall. With low pressures and *small* currents, the current density may fall off to zero at the outer zones of the cathode, but as in such cases the utility of a guard-ring is questionable, we are not concerned with these conditions. With higher pressures and small currents through the tube the glow may disappear, not from the outer edges of the cathode, but from one side, and consequently the current density to the outer rings again

Fig. 2.



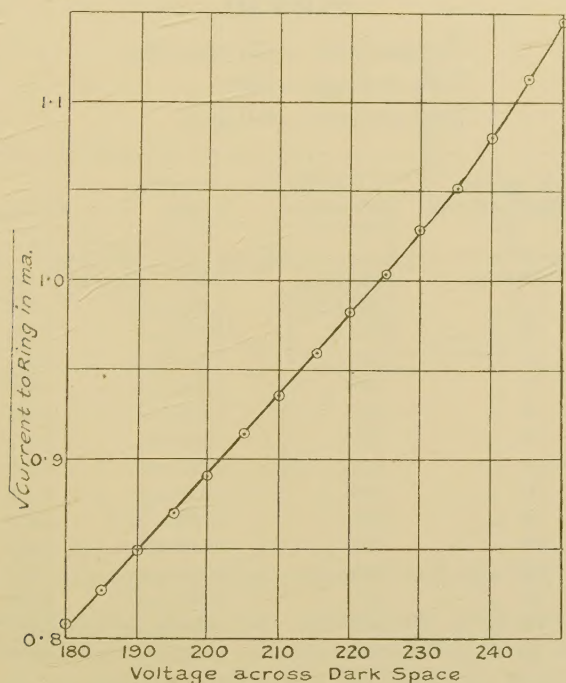
appears to decrease, although actually it may really increase.

With the information gained from these experiments, it was decided to construct the new tube with a cathode of radius about 1.5 cm. surrounded by a guard-ring of diameter 7.0 cm.

While the split-cathode tube was in use, it was decided to conduct some experiments to find out in what way the current to any ring depended upon the potential difference between that ring and the negative glow boundary of the cathode dark space. It was hoped that by keeping all the rings but one at a constant potential, the thickness of

the dark-space would be unaffected by the variation of the potential of the one, and thus the dependence of current on the P.D. across the dark-space alone would be ascertained. Each ring in turn was made more and more positive with respect to the remainder of the cathode, and as any possible change in dark-space thickness would have been an increase, it was impossible to observe through the glow over the other rings whether or not any such change took place.

Fig. 3.



This experiment is admittedly open to very strong criticism, but the results, taken in conjunction with more reliable evidence, may be regarded as having some weight. At the lower pressures, the current-voltage relation was found to approximate to Aston's law (equation 3). Fig. 3, drawn from Table III. is a curve obtained by plotting the square root of the current to ring No. 3 against the potential difference across the dark-space. This example was taken at random from the low-pressure curves,

since they all exhibited the same characteristics. As will be seen, the curve is very nearly a straight line over the greater part of its range. This range could not be extended owing to arcing taking place between the ring and its neighbour when the potential difference between them was large.

Whatever law the voltage-current curve obeyed at high pressures, it was certainly not Aston's law, but seemed to involve an even lower power of C .

TABLE III.

Gas-pressure = 53 mm. Hg.

Tube voltage = 250.

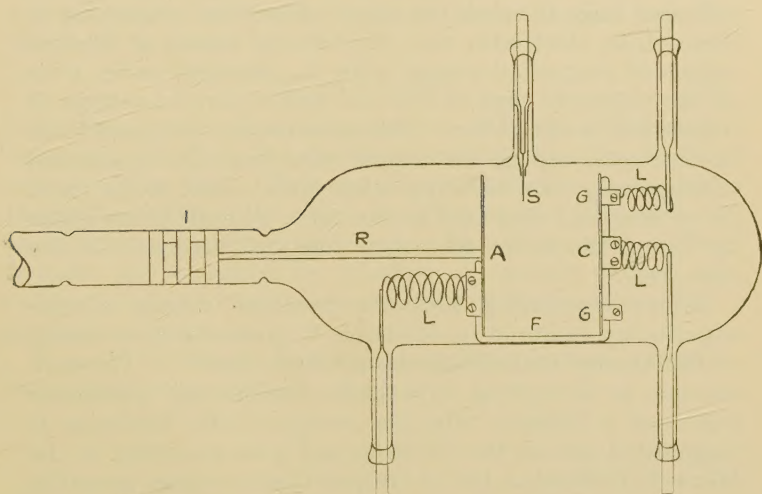
Tube current = 6.0 m.a.

| P.D. between ring and cathode. (v.) | P.D. across dark-space. (250 - v.) | Current to ring. (C.) | \sqrt{C} (m.a.) ^{1/2} . |
|---|--|-----------------------------|------------------------------------|
| 0 volts. | 250 volts. | 1.312 m.a. | 1.145 |
| 5 " | 245 " | 1.242 m.a. | 1.113 |
| 10 " | 240 " | 1.172 m.a. | 1.081 |
| 15 " | 235 " | 1.112 m.a. | 1.051 |
| 20 " | 230 " | 1.059 m.a. | 1.029 |
| 25 " | 225 " | 1.011 m.a. | 1.003 |
| 30 " | 220 " | 0.964 m.a. | 0.982 |
| 35 " | 215 " | 0.921 m.a. | 0.959 |
| 40 " | 210 " | 0.876 m.a. | 0.936 |
| 45 " | 205 " | 0.836 m.a. | 0.914 |
| 50 " | 200 " | 0.796 m.a. | 0.891 |
| 55 " | 195 " | 0.759 m.a. | 0.870 |
| 60 " | 190 " | 0.721 m.a. | 0.849 |
| 65 " | 185 " | 0.686 m.a. | 0.827 |
| 70 " | 180 " | 0.651 m.a. | 0.807 |

This may be due to the fact that the thickness of the dark-space is small at the higher pressures and current densities, and consequently any alteration in thickness would have a greater relative effect on the current passing to the ring. One very curious phenomenon observed at a pressure of 1.24 mm. Hg. was the manner in which the central disk was affected by changes of potential of its neighbour. A marked discontinuity was found in the voltage-current curve for ring No. 2, the current

suddenly falling to a very small amount. It was observed that at this discontinuity, which occurred when the P.D. between the ring and the remainder of the cathode was about 8 volts, the glow disappeared, not only from above ring No. 2, but also from above the central disk, or ring No. 1. The tube current in this case was again 10 m.a. Similar effects were observed when the split electrode was the anode of the discharge-tube.

Fig. 4.



Construction of Experimental Discharge-tube.

Having found from the preliminary experiment the relative sizes of cathode and guard-ring necessary to make such an arrangement effective, an electrode system was designed and constructed as shown in fig. 4.

An anode of nickel A, 7 cm. in diameter, was separated from the cathode C (diameter 2.98 cm.) and guard-ring G (external diameter 7 cm.) by a glass framework F, the fastenings being small nickel clips silver-soldered to the electrodes and clamped to the glass rods. The distance between the anode and cathode was 5.1 cm. A nickel rod R was riveted to the centre of the anode, the other end being screwed into an iron armature I, provision thus being made for moving the electrode system as a whole by means

of an external electromagnet. The armature was designed to slide in a glass tube, which it fitted fairly well, its movement being restricted by constrictions in the tube. This was necessary to prevent the whole system falling into the discharge-tube and causing damage there. Grooves were turned round the circumference of the iron and along its length, so that air might be pumped out past it. These grooves were important, not so much from the point of view of pumping speed, as from the fact that if the tube was exhausted too rapidly, a solid armature was found to act like a piston, being driven along the tube with sufficient force to crack the glass. Electrical connexion to these three electrodes was effected by means of flexible spirals of enamelled copper wire, L, clamped under nuts on the electrode clips at one end and soldered to strips of copper foil at the other. Phosphor-bronze wire could not be obtained, and as the copper wire was soft, longer and consequently less self-supporting spirals had to be used. No sealing-wax was used in the tube, all seals being made by fusing the strips of copper foil into the ends of the side-arms.

Before proceeding with the practical details of the experiment, it would be advisable to give a brief summary of the theory underlying the methods used⁽⁷⁾. We may assume, as a working hypothesis, that in any particular region of a Geissler tube the energy of the discharge is distributed among the electrons and ions according to the Maxwell-Boltzmann law, corresponding to a space potential v_s with respect to the anode. If a probe or sounding electrode is inserted into this region and is maintained at a potential v with respect to the anode, then a current will flow to the probe and will change as v is varied. Owing to the mobility of the electrons being much greater than that of the positive ions, the condition that $v=v_s$ is not in general satisfied when the current to the sound electrode is zero. If we vary v and plot a current-voltage curve, the resulting "characteristic" may be split up into three sections. When the sound is very strongly negative with respect to the space potential, the current is carried by positive ions alone, practically all the electrons being rejected. When the sound is but slightly negative, positive ions are still accelerated to the collector, but also the faster electrons are not retarded sufficiently to prevent them from contributing to the total current. As v

approaches the value v_s , the positive-ion current becomes negligible compared with the electron current, although the latter is still carried by retarded electrons. Finally, when v is positive with respect to v_s , the electrons are accelerated, and the current becomes so large that the main discharge is affected, the energy distribution no longer being truly Maxwellian.

The first part of the curve is of importance in this experiment, only in so far as it allows us to make a correction for the positive-ion current to the second part, thus giving us the true electron current. If i_+ is the current due to accelerated positive ions, the first part of the curve is of the form :

$$i_+^2 \propto 1 + ve/kT, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which e is the charge on the ion, k is the Boltzmann constant, and T is the temperature corresponding to the energy of the ions. This equation only holds good when the radius of the probe wire is small compared with that of the sheath of positive ions which is formed round it. The straight line obtained by plotting i_+^2 against v may be extrapolated to correct the second part of the characteristic, as mentioned above.

It may be shown that the retarded electron current varies with v according to the law :

$$i_- = IA\epsilon^{\frac{(c-v_s)e}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where I is the electron current density in the discharge, and A is the area of the sound electrode; e and T have their previous significance, but this time they refer to electrons and not to positive ions. From this equation we can derive the form :

$$\log i_- = \text{constant} + \frac{(v-v_s)e}{kT}, \quad . \quad . \quad . \quad . \quad (7)$$

and if $\log i$ is plotted against v , the result should be a straight line of slope e/kT . This is born out in practice, which justifies the original assumption as to the distribution of energy between the electrons.

The third part of the characteristic, dealing with the accelerated electrons, again obeys a law of the form given by (5). Consequently, if the logarithm of the corrected electron current is plotted against the potential of the

sound electrode the result is a curve which departs from a straight line at the space potential. This is a very convenient method, which is used in the experiment described here to find the space potential at the negative glow boundary of the cathode dark-space. Applied as a correction to the tube voltage, this gives the difference of potential existing across the dark space.

The dimensions of the sound electrode (S in fig. 4) were arrived at from the following considerations. The plane electrode is particularly good as a sound, as the "kink" at the space potential in the semi-log curve is well defined. Since, however, a very small region was investigated in this experiment, such an electrode was obviously ruled out. For this reason, among others, the sphere was also rejected. By process of elimination the cylindrical form was chosen, the probe being molybdenum wire, .015 cm. in diameter. Wire of this small size was chosen because when a cylinder of large radius is used the accelerated positive-ion current is not limited by orbital motion, but by space-charge, and equation (5) no longer holds good. This means, of course, that the sound-current cannot be corrected for the positive-ion contribution in order to get the true electron current. There is also, of course, the same objection to a cylinder of large radius as there is to a plane.

A short length of molybdenum wire was pinched into the end of a short copper rod, which was in turn silver-soldered to a strip of copper foil for sealing-in purposes. The whole was sheathed in a glass tube which was drawn down to a small bore at one end, through which 1.28 cm. of the molybdenum wire was allowed to protrude. Care was taken that the wire did not touch the glass at the point where it emerged from the sheath.

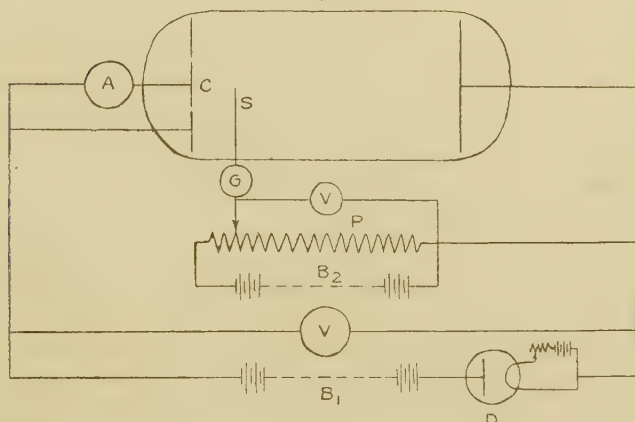
The electrical connexions were as shown in fig. 5. The discharge was maintained by a large battery of lead storage cells, B_1 the current being regulated by a saturated diode D. This arrangement has the great advantage that, provided the diode is of the bright emitter type, the current it passes is independent of slight fluctuations in the battery voltage, and may readily be varied by adjusting the filament current by means of a rheostat. The current to the cathode C produced by a potential difference V was measured by a milliammeter A. A varying potential v was applied to the sound by means of another battery B_2 and a potentiometer P, the resulting current being

measured by a shunted galvanometer G. Before the apparatus was used, the insulation between the guard-ring and the cathode was tested to ensure that the currents to them did not mix before they were measured.

In order to find the thickness of the dark-space, an accurate sighting tube as used by Aston was employed. At the eye end was a pinhole, the object end being fitted with a pointer. This tube was mounted on a base which slid along a scale mounted parallel to the discharge-tube.

A Gaede annular jet mercury-vapour pump, backed by a Cenco Hyvac pump, served to exhaust the tube to a pressure immeasurable by a large McLeod gauge (at the

Fig. 5.



most 10^{-5} mm. Hg.). Owing to the copper-to-glass seals it was unsafe to bake out the tube, and it was necessary to rinse it out several times with the gas to be used to ensure purity. The first gas used was hydrogen, admitted by a hot palladium tube, but the dark-space was found to be so ill-defined that it was soon abandoned. Neon was then tried, the purest specimen obtainable having a composition of 98 per cent. neon and 2 per cent. helium. Although the boundary of the dark-space was still somewhat diffuse under certain conditions of pressure and current density, yet its colour was bluish as distinct from the pink of the negative glow, and its thickness could generally be measured by the sighter to within 2 per cent.

The gas was stored in a reservoir over water, and was admitted to the discharge-tube by sharing a volume at

high pressure, contained in the space between two taps sealed close together, with a large evacuated bulb. A small portion of the gas in the bulb was then shared in a similar manner with the discharge-tube, final adjustment being effected by pumping.

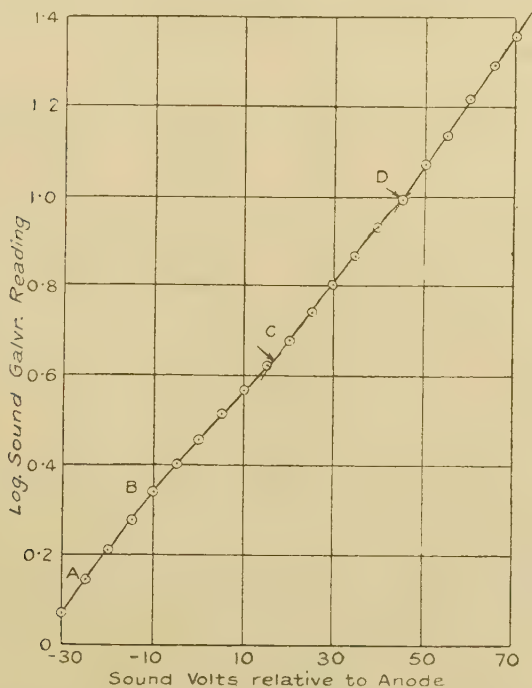
The use of liquid-air traps between the discharge-tube and the rest of the apparatus effectually prevented the entry of mercury vapour from the McLeod gauge and the pump.

The procedure adopted during the taking of a set of readings was as follows. A suitable pressure of neon and value of tube current having been obtained in the tube, the sighting-tube was laid on the probe, and by careful manipulation of an electromagnet the electrode system was shifted along the discharge-tube until the boundary of the dark-space coincided with the sound in the field of view. A current-voltage characteristic was then taken, and the space potential of the boundary was found and applied to the tube voltage as a correction. The sighting-tube was next laid on the cathode, the difference of the two readings giving the thickness of the dark-space. In this way the four quantities necessary to test Aston's law were obtained, viz. gas-pressure, current density, thickness of the dark-space, and the potential difference across it.

Unfortunately, it was found that the positive-ion current to the sound-electrode in the region investigated did not obey the law expressed in equation 5, and as a consequence the true electron current was an unknown quantity. The logarithm of the total current was plotted against the potential of the probe, and fortunately the electron current was sufficiently in excess of the positive-ion contribution to nullify the effect of the latter on the straightness of the line obtained over the greater part of the curve, as will be seen by reference to fig. 6. This is a typical "semi-log" curve, and it will be noticed that the affected part of the curve is satisfactorily distant from the kink indicating the space potential (C). In the neighbourhood of the dark-space the curves exhibit an upward tendency after the space potential has been reached, as is shown by the section CD. The rapid increase of current beyond the point D is due to ionization by collision taking place in the electron sheath surrounding the sound electrode, a state of affairs which seemed to set in gradually at low

pressures and current densities, and taking the form of violent arcing at the higher pressures. The curve shown in fig. 6 is of the type to be expected in the neighbourhood of the cathode dark-space. Normally the "semi-log" curve becomes more horizontal after the space potential has been reached, but Emeléus ⁽⁸⁾ found an upward tendency after the "kink," as shown at C (fig. 6) when the exploring electrode was near the dark-space.

Fig. 6.

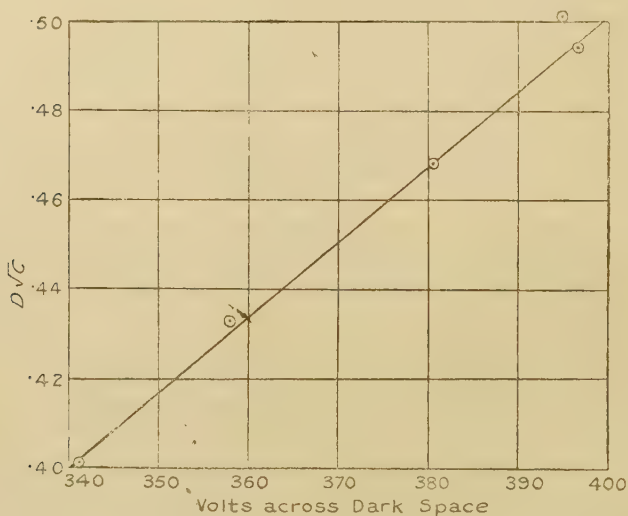


At the point D it was noticed that a faint red glow appeared at the top of the sound-wire where it emerged from the glass sheath, and as the potential was increased this glow gradually spread and increased in brightness. The space potential, it will be observed, is 16 volts *positive* with respect to the anode. This indicates that the electron concentration gradient was sufficiently great to allow a drift current to flow against the electric field in the negative glow. Here we differ from Aston, who would

have assumed in this case that the potential difference between the cathode and the boundary of the dark-space was the same as the tube voltage, viz. 345 volts, whereas it was actually 361 volts, a difference of 3 per cent. This should not be a sufficiently large error to cause any material difference between the results of the present investigation and those of Aston's original experiments, and actually very little difference was observed.

Several pressures of neon were tried in an attempt to obtain an extensive range of tube currents, for, as a rule, the low current densities were productive of curved and diffuse dark-space boundaries, and large currents were

FIG. 7.



accompanied by the striking of the discharge to the back of the cathode. The former type of discharge, not entirely covering the cathode, probably rendered the guard-ring inoperative, and the latter type was entirely useless. When suitable discharges were obtained, the results of the experiments were plotted in the manner shown in fig. 7 and Table IV. The abscissa is the P.D. across the dark-space, while the product of the dark-space thickness and the square root of the current to the cathode is the ordinate.

The one bad point was the result of a discharge which appeared to be extremely unstable, although when tested

with a wavemeter and also with a detector circuit coupled to a coil in the anode lead, no trace of oscillatory current was found.

The straight line fits in very well with (3), and the constant G has a value of 113 volts. This is about 25 volts in excess of Aston's value, but the discrepancy is doubtless due to the correction for the potential of the dark-space boundary, in the present work.

TABLE IV.

Gas-pressure = 0.33 mm. Hg.

| Tube volts. V. | Boundary potential. v_g . | P.D. across dark-space. | Dark-space thickness. D. | Current to cathode. C. | $D\sqrt{C}$. |
|----------------------|-----------------------------------|----------------------------|--------------------------------|------------------------------|---------------|
| 380 | 16.5 v. | 396.5 v. | 0.9 cm. | 0.3 m.a. | .494 |
| 370 | 25.0 v. | 395.0 v. | 1.02 cm. | 0.25 m.a. | .509 |
| 358 | 22.5 v. | 380.5 v. | 1.06 cm. | 0.195 m.a. | .468 |
| 345 | 13.0 v. | 358.0 v. | 1.12 cm. | 0.15 m.a. | .433 |
| 327 | 14.0 v. | 341.0 v. | 1.27 cm. | 0.10 m.a. | .401 |

Discussion of Results.

Whenever definite evidence has been forthcoming to help us to decide between Aston's law and the Langmuir space-charge law, the decision has always been in favour of the former. This, perhaps, is not surprising, for the space-charge theory was developed for the case of electron emission in high vacuum, no allowance being made for collisions between the electrons and gas molecules. McCurdy⁽⁹⁾ has extended this simple theory to cover the case of an electron making so many collisions that it reaches a limiting velocity. The current in this case is still proportional to $V^{3/2}$. It is probable that of these extremes of condition neither are to be found in the cathode dark-space.

Compton⁽¹⁰⁾ has shown that the assumption of space-charge limitation is more defensible with the abnormal cathode fall than in the case of the normal, for which he has developed a new theory. That the current in the former type of discharge is not so limited has been shown in this paper. It is possible that the primary dark space⁽¹¹⁾

discovered by Aston in certain gases is a sheath of space-charge of the type discussed above, as its thickness is so small that a current carrier would have little opportunity of making a collision in its journey across; but the knowledge of this possibility does little to solve the problem of the mechanism of conduction of electricity across the Crookes's dark-space.

It may be remarked here that the visual measurement of the dark-space thickness is contrary to the opinions of Seeliger and Lindow⁽¹²⁾, who have pointed out that the eye estimates the region of maximum light-intensity gradient to be the boundary of the dark-space, the thickness thus measured being perhaps as little as 50 per cent. of the distance from the cathode to the region of maximum light-intensity. There would seem to be little reason for defining the dark-space on the latter basis, but rather to define the boundary as the region of minimum electric field⁽¹⁰⁾. This region has been found by some workers in this field⁽⁶⁾ to correspond at least approximately to the visual boundary, and certainly would not yield a dark-space thickness in excess of that observed by means of the sighter.

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- (7) See (3) above,
- (8) Emeléus, Proc. Camb. Phil. Soc. xxiii. p. 531 (1926).
- (9) McCurdy, Phys. Rev. xxvii. p. 157 (1926).
- (10) Compton and Morse, Phys. Rev. xxx. p. 305 (1927).
- (11) Emeléus and Carmichael, Phil. Mag. v. p. 1039 (1928).
- (12) Seeliger and Lindow, *Phys. Zeit.* xxvi. p. 393 (1925).

L. The Hall Effect, Electrical Conductivity, and Thermo-electric Power of the Lead-Antimony Series of Alloys.
 By EMLYN STEPHENS, M.Sc., Physics Department,
 University College of Swansea *.

Introduction.

THERE is no satisfactory theoretical explanation of electrical conduction and the galvanomagnetic effects in metals and alloys, and further knowledge of the various phenomena is still necessary. A great deal of the earlier experimental work has been carried out with impure materials, and it is well known that some physical properties are found to show large variations with a slight trace of impurity.

In two previous papers † the variation of electrical properties with composition of two series of alloys in which compounds are formed have been discussed. The object of the present work was to study the variation of the Hall effect, electrical conductivity, temperature coefficient of resistance, and thermoelectric power with composition of a series of alloys which shows no extreme variation of crystal structure over a large range of composition. The examination of the properties of this series is important from a theoretical standpoint, and in a further paper the electrical properties of the three series will be discussed in relation to theory. According to the equilibrium diagram‡ of the Pb-Sb alloys, a solid solution of Sb in Pb is formed up to about 2 per cent. by weight of Sb, but all other alloys consist of a eutectic mixture of this solid solution and Sb crystals.

The determinations of the electrical resistivity, temperature coefficient of resistance, thermoelectric power, and Hall coefficient have been made for the same specimen. The alloys required annealing, as their electrical properties depend on their physical state. In the present experiments the electrical resistivity was determined for the alloys after preparation, and was afterwards redetermined for each alloy after annealing at a suitable temperature.

* Communicated by Prof. E. J. Evans, University College of Swansea.

† Stephens and Evans, *Phil. Mag.* vii. Jan. 1929; Stephens, *Phil. Mag.* viii. Sept. 1929.

‡ International Critical Tables, ii.

This was repeated until further annealing produced no change in the resistivity. The other properties were then determined for the alloys in this final state.

Matthiessen* and Smith† have determined the electrical conductivity curve of the Pb-Sb system of alloys, and the latter investigator also measured the thermal conductivities of these alloys and discussed his results in relation to the Wiedmann-Franz law. The curve connecting thermoelectric power and composition of the alloy was determined by Rudolfi‡, and measurements of the electrical conductivity and thermoelectric power of annealed specimens of these alloys were made by Broniewski and Sliwowski§, who were engaged in a study of the equilibrium diagram of the Pb-Sb system.

Experimental Arrangement.

The experimental arrangements used in the present work have been described in an earlier paper||, so that a brief description here will be sufficient.

The alloys were made from very pure metals, the lead and antimony containing ·0043 per cent. and ·084 per cent. impurities respectively. The impurities in the lead were : silver ·0005 per cent., antimony ·0005 per cent., copper ·0003 per cent., bismuth ·0015 per cent., iron ·0012 per cent., and zinc, ·0003 per cent., while the impurities in the antimony were : iron ·041 per cent., lead ·025 per cent., copper ·012 per cent., sulphur ·003 per cent., and arsenic ·003 per cent. The alloys were chill cast in the form of plates, some in a graphite mould 15 cm. long, 2·0 cm. wide, and ·4 cm. thick, and the others in an iron mould 15 cm. long, 3·0 cm. wide, and ·4 cm. thick. The antimony plate cast in the iron mould was composed of small crystals, and in order to study the possible effect of crystal size on the Hall coefficient a second plate, consisting of large crystals, was made by allowing the molten metal to cool in a hot sand mould.

Altogether 10 plates were cast, of the following percentage composition by weight :—(1) 100 per cent. Pb ; (2) 96 per cent. Pb, 4 per cent. Sb ; (3) 90 per cent. Pb,

* Pogg. *Ann.* cx. p. 28 (1860).

† Phys. Rev. xxiii. p. 307 (1924).

‡ *Zeit. Anorg. Chem.* lxvii. p. 65 (1910).

§ *Rev. de Met.* xxv. p. 397 (1928).

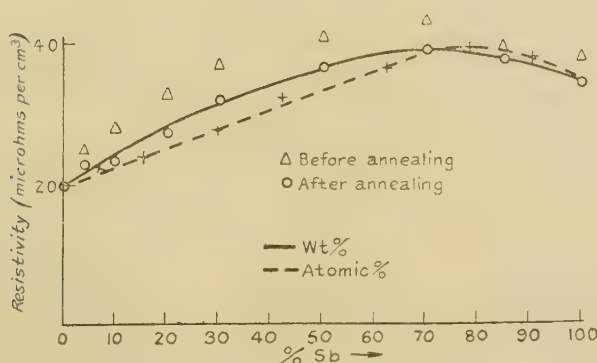
|| Stephens, *loc. cit.*

10 per cent. Sb ; (4) 80 per cent. Pb, 20 per cent. Sb ; (5) 70 per cent. Pb, 30 per cent. Sb ; (6) 50 per cent. Pb, 50 per cent. Sb ; (7) 30 per cent. Pb, 70 per cent. Sb ; (8) 15 per cent. Pb, 85 per cent. Sb ; (9) and (10) 100 per cent. Sb.

(a) *Electrical Resistivities and Temperature Coefficients of Resistance of the Alloys.*

The electrical resistivity was determined by fixing a plate of the alloy across two knife-edges, and determining the resistance of a known length by means of the Kelvin Bridge. The determinations before and after annealing were made at 0° C., and the values of the resistivities in

GRAPH I.



the initial and final states of the alloy are given in Table I. and Graph I.

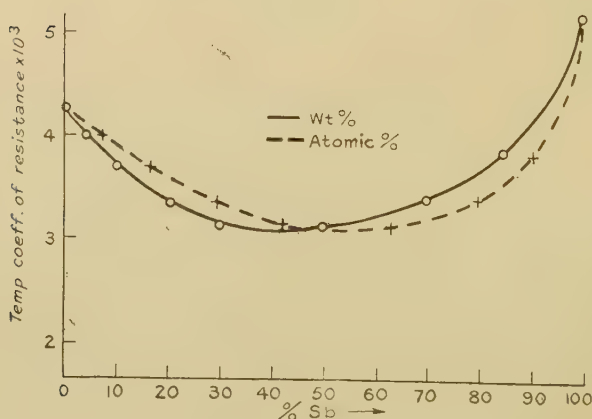
The mean temperature coefficient of resistance over the range of temperature between 0° C. and 100° C. was determined for each alloy in its final state only, and these results are given in Table I. and Graph II. The resistance of a length of plate of these alloys could be determined with an accuracy of about 1 in 800, but as the determination of the resistivity also involved measurements of the thickness and width, the accuracy of the resistivity determinations is about $\frac{1}{3}$ of one per cent. The determination of the temperature coefficients did not involve any measurements of the dimensions of the plates, and it is considered that the temperature coefficients are also accurate to within about $\frac{1}{3}$ per cent.

TABLE I.

| Composition of alloy by weight. | Resistivity before annealing, in microhms per cm. ³ | Resistivity after annealing, in microhms per cm. ³ | Mean temp. coeff. of resistance between 0° C. and 100° C. $\times 10^4$. |
|---------------------------------|--|---|---|
| 100 % Pb | 19.6 | 19.6 | 42.7 |
| *96 % Pb, 4 % Sb ... | 24.95 | 22.73 | 40.2 |
| 90 % Pb, 10 % Sb ... | 27.8 | 23.82 | 37.1 |
| 80 % Pb, 20 % Sb (a) | 33.0 | 27.4 | 33.6 |
| *80 % Pb, 20 % Sb (b) | 33.1 | 27.7 | — |
| 70 % Pb, 30 % Sb ... | 37.1 | 32.3 | 31.4 |
| 50 % Pb, 50 % Sb ... | 41.0 | 36.7 | 31.3 |
| 30 % Pb, 70 % Sb ... | 43.3 | 39.4 | 33.8 |
| *15 % Pb, 85 % Sb ... | 39.7 | 38.3 | 38.2 |
| 100 % Sb ... | 38.5 | 35.3 | 51.4 |

* Annealed in vacuum.

GRAPH II.



(b) Thermoelectric Power of the Alloys.

The thermoelectric powers of the alloys were determined with copper leads soldered to the ends of the plates. One junction was enclosed in steam while the other was kept at the temperature of running tap-water. The thermo-E.M.F. over this range of temperature was

determined by means of a Tinsley vernier potentiometer, and the values of the thermoelectric powers in microvolts per degree centigrade with respect to both copper and lead are given in Table II. and Graph III. Repeated determinations of the thermoelectric power of the copper-alloy couples made when the temperature of the cold junction was varied over a range of several degrees were in good agreement, so that the relation between E.M.F. and temperature was probably linear between room-temperature and 100° C.

TABLE II.

| Composition of alloy by weight | Thermoelectric power with respect to Cu, in microvolts per degree centigrade. | Thermoelectric power with respect to Pb, in microvolts per degree centigrade. |
|-----------------------------------|--|--|
| 100 % Pb | -3.16 | 0 |
| 96 % Pb, 4 % Sb | -2.67 | + .49 |
| 90 % Pb, 10 % Sb | -2.30 | + .86 |
| 80 % Pb, 20 % Sb | - .62 | + 2.54 |
| 70 % Pb, 30 % Sb | +1.15 | + 4.31 |
| 50 % Pb, 50 % Sb | +3.21 | + 6.37 |
| 30 % Pb, 70 % Sb | +2.20 | + 5.36 |
| 15 % Pb, 85 % Sb | +2.46 | + 5.62 |
| 100 % Sb | +38.0 | +41.16 |

(c) *Hall Effect of the Alloys.*

A transverse magnetic field produces a rotation of the equipotential lines in a plate carrying an electric current, so that a difference of potential is set up between the edges of the plate. This transverse galvanomagnetic potential difference, E , is given in abs. units by the formula

$$E = \frac{RHI}{d},$$

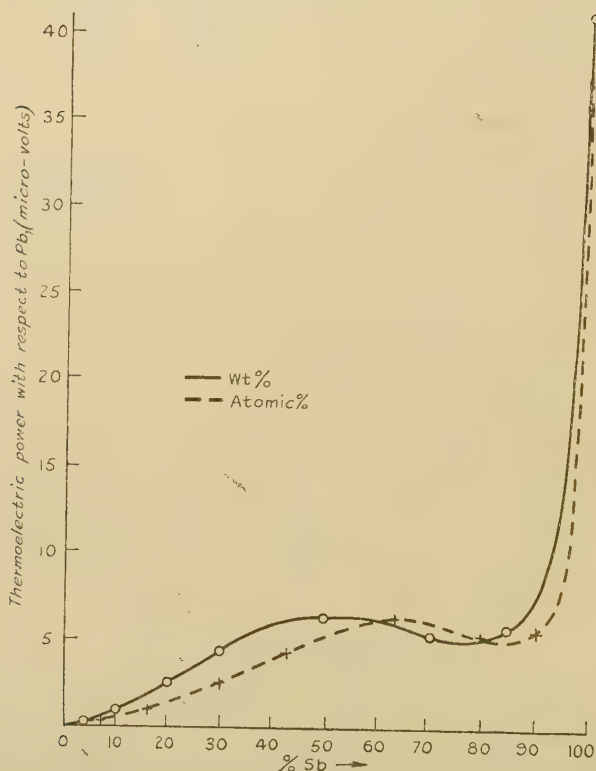
where H is the magnetic field in gauss, I the current in abs. units, d the thickness of the plate in cm., and R the Hall coefficient.

This coefficient R , which depends on the temperature and, also, for some metals, on the intensity of the magnetic

field, has different signs in various metals. The Hall coefficient is +ve for both antimony and lead, the value for lead being about .05 per cent. that for antimony.

Although the Hall effect for antimony is very large, it is small for some of the Pb-Sb alloys, and a very sensitive galvanometer was required to measure the P.D. The

GRAPH III.



delicate Paschen galvanometer used in the present experiments was mounted on a stone pillar at a distance of $7\frac{1}{2}$ metres from a large circular electromagnet which had been rotated into such a position that its effect on the galvanometer was a minimum. Magnetic fields ranging from 3088 gauss to 8468 gauss could be obtained in the 1.5 cm. air-gap between the pole-pieces when the electromagnet was excited by currents varying from 1 ampere to 6 amperes.

The alloy plate under investigation was rigidly fixed in a vertical position in the magnetic field by two brass clamps which also served as leads for the primary current. These clamps were fixed to a wooden frame which also supported the secondary electrodes, consisting of spring copper contacts carried by bars of ebonite. These electrodes, which could be moved vertically along the edges of the plate by means of a screw arrangement, were connected to the galvanometer by long, well insulated, flexible wires. These wires were pulled taut so as to eliminate the effects of vibration as far as possible.

In a determination of the Hall coefficient, the secondary electrodes were adjusted on an equipotential line. Then, with the secondary circuit closed, no deflexion is produced in the galvanometer when the primary current is reversed, but on applying the magnetic field, and again reversing the current, with the secondary circuit closed, a deflexion due to the Hall P.D. between the edges of the plate is produced in the galvanometer. The Hall P.D. was determined for several values of the magnetic field up to 8500 gauss, and a graph drawn showing the relation between the P.D. and magnetic field. The value of $\frac{E}{H}$ determined from this graph was then used to calculate the Hall coefficient from the equation $R = \frac{Ed}{HI}$.

The primary current (4 amps.) passing through the plates of high lead content could be read on a Weston ammeter with an accuracy of about 1 in 1200, and the minimum current (1 ampere) used for the antimony plate and the alloys of high antimony content could be read with an accuracy of about 1 in 300. This ammeter was periodically calibrated by comparison with a large Weston Standard Ammeter.

The magnetic fields corresponding to various currents passing through the electromagnet were determined by means of a Grassot fluxmeter with an accuracy of about 1 in 250. The fluxmeter and search-coil were calibrated by means of a delicate ballistic galvanometer and a search-coil of known mean area.

The Hall effect was determined at room-temperature, the exact temperature being observed by a thermometer suspended with its bulb in contact with the plate.

The experimental results for the Hall coefficients are given in Table III. and Graph IV.

In addition to the Hall potential difference, a transverse galvanomagnetic temperature difference is set up between the edges of the plate. This is the Ettingshausen effect, and the difference of temperature, ΔT , is given by

$$\Delta T = \frac{P.H.I}{d},$$

where H is the magnetic field in gauss, I the current in absolute units, d the thickness of the plate in cm., and P the Ettingshausen coefficient.

TABLE III.

| Composition of alloy by weight | Hall coefficient. | Temperature ° C. |
|-----------------------------------|----------------------|---------------------|
| 100 % Pb | +·00009* | 20·0 |
| 96 % Pb, 4 % Sb... | +·000997 | 19·6 |
| 90 % Pb, 10 % Sb... | +·00324 | 17·4 |
| 80 % Pb, 20 % Sb... | +·00429 | 18·7 |
| 70 % Pb, 30 % Sb... | +·00530 | 20·1 |
| 50 % Pb, 50 % Sb... | +·0112 | 20·3 |
| 30 % Pb, 70 % Sb... | +·0333 | 20·3 |
| 15 % Pb, 85 % Sb... | +·0876 | 17·8 |
| 100 % Sb... | +·213 | 17·8 |

* Campbell, 'Galvanomagnetic and Thermomagnetic Effects.'

If the secondary electrodes in the Hall-effect determinations are not made of the same material as the plate itself, the Ettingshausen temperature difference ΔT set up between the edges of the plate will result in a thermo-E.M.F. $\theta . \Delta T$ in the secondary circuit, where θ is the thermoelectric power of the electrode with respect to the plate. Therefore the total potential difference as measured by the galvanometer in the Hall-effect determination is given by

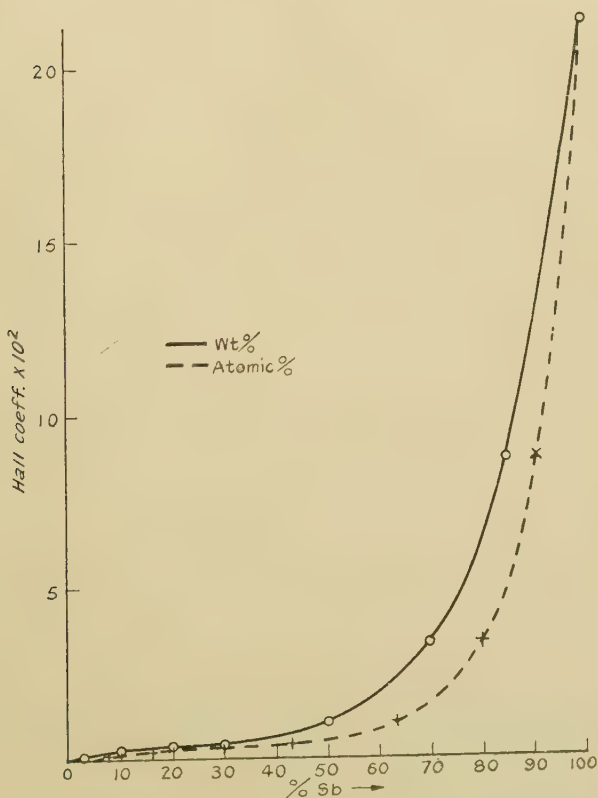
$$E = E_H \pm \theta . \Delta T,$$

where E_H is the true Hall P.D., and the Hall coefficient becomes

$$R = \frac{E \times d}{H \times I} \pm P . \theta .$$

As a result of special experiments, it was found that the Ettingshausen effect for the alloys was inappreciable, and the Hall coefficients have been determined within 1 per cent. In the case of antimony, the use of copper electrodes made accurate measurements of the Hall coefficient rather difficult, owing to the heat generated

GRAPH IV.



by the magnet and the large thermoelectric power of copper with respect to antimony. This difficulty was overcome by employing antimony electrodes, and in addition the Ettingshausen effect was practically eliminated.

All the alloys were annealed at the same temperature, 232° C., in an electric furnace, an atmosphere of coal-gas being used to prevent oxidation. A few alloys were

annealed with the furnace evacuated to about $\frac{1}{10}$ mm. pressure, and the results are in agreement with those obtained for the alloys annealed in coal-gas. The annealing was performed in periods of 15 hours, and the furnace was allowed to cool before removing the alloy.

Discussion of Results.

The curves showing the relation between the resistivity, temperature coefficient of resistance, thermoelectric power, Hall effect and the concentration of Sb in the alloy are all continuous, and furnish no irregularities or singular points. These curves, as would be expected, are in distinct contrast to those obtained for a series of alloys in which compounds are formed.

If the alloys were purely mixtures of lead and antimony, the electrical resistivity would be expected to vary uniformly with the composition by volume. The resistivity of the alloy formed by the addition of lead to pure antimony is greater than that for the pure antimony, although lead is a better conductor than antimony. The alloy of maximum resistivity has a composition of about 28 per cent. by weight of lead, but a further increase in the lead content of the alloy produces a regular diminution in the resistivity. Broniewski and Sliowski* also find a maximum corresponding to 28 per cent. by weight of lead in their resistivity-composition curve, but the value of the resistivity determined by them is about 5 per cent. higher. The resistivity of the antimony used in the present experiments was 2 per cent. lower than that determined by Broniewski and Sliowski.

The temperature coefficient of resistance of pure antimony is very large, being about 25 per cent. greater than that for lead. The purer the metal, the greater is its temperature coefficient of resistance, and for many metals the addition of only a trace of foreign metal diminishes the temperature coefficient considerably. Probably in this case the diminution in the temperature coefficient is caused by the introduced metal forming a solid solution with the pure metal. With the addition of pure lead to antimony the temperature coefficient of resistance at first diminishes rapidly, and 3 atoms per cent. of lead is sufficient to

* *Loc. cit.*

diminish it by about 17 per cent. The minimum temperature coefficient (31.0×10^{-4}), is obtained for an alloy having a composition of about 47 atoms per cent. lead. The value of the temperature coefficient does not differ much from this minimum value over the range of composition from 38 atoms per cent. Pb to about 54 atoms per cent. Pb. This minimum temperature coefficient for the Pb-Sb alloys is much greater than the minimum obtained for the Cu-Sb* and Cu Sn† series of alloys, in which there are extreme changes of crystal structure, and it seems as if the temperature coefficient of resistance is intimately connected with the structure.

An examination of the four graphs given in the present paper does not indicate any close connexion between the phenomena. The addition of a small quantity of lead to antimony diminishes the thermoelectric power by a far greater amount than the Hall effect, and further addition of lead does not produce similar variations in these effects. The addition of 5 atoms per cent. of lead is sufficient to diminish the thermoelectric power of antimony by about $\frac{4}{5}$ ths of its initial value, but the Hall coefficient for this alloy is about 75 per cent. of that for pure antimony. This decrease in the thermoelectric power caused by the addition of lead is maintained until the composition of about 15 atoms per cent. of lead is reached. Further addition of lead produces an increase in thermoelectric power until a maximum is attained corresponding to the composition of 35 atoms per cent. of lead, which is followed by a gradual diminution in thermoelectric power. The form of this thermoelectric power-composition curve is similar to that obtained by Broniewski and Sliwowski‡.

Graph IV., showing the relation between the Hall coefficient and composition of the alloy, is very interesting. The addition of antimony to lead produces a small increase in the Hall coefficient until the composition of 20 atoms per cent. of antimony is reached. Between compositions of 20 and 50 atoms per cent. of Sb, a very small increase in Hall coefficient which is practically proportional to the change in composition is obtained. With further addition of antimony the Hall coefficient increases more rapidly, being about half that of antimony for an alloy containing

* Stephens and Evans, *loc. cit.*

† Stephens, *loc. cit.*

‡ *Loc. cit.*

6 atoms per cent. of lead. In alloys of high antimony content, practically all the antimony in the alloy is present as pure crystals, and so the Hall coefficient for an alloy of, say, 50 atoms per cent. of Sb would be expected to be about half that of pure antimony. This alloy has a Hall coefficient of only $2\frac{1}{2}$ per cent. of that of pure antimony, and it seems as if there is some inter-crystal force opposing the effect of magnetism.

According to the magnetic susceptibility-composition curve for the Pb-Sb alloys determined by Honda and Endo *, the addition of about 5 per cent. of lead to antimony reduces the susceptibility of antimony to about one-half its original value. With further addition of lead the susceptibility diminishes linearly to the value for pure lead. Although the Hall coefficient-composition curve is somewhat similar in form to the susceptibility curve, there does not seem to be any intimate relation between them.

TABLE IV.

| | | | | | | |
|---------------------|-------|-------|-------|-------|-------|-------|
| Magnetic field ... | 3088 | 4632 | 5789 | 6833 | 7704 | 8468 |
| Hall coefficient... | +·232 | +·232 | +·234 | +·232 | +·229 | +·217 |

Mean temperature=16·3° C.

The Hall coefficients for all the alloys examined did not vary with change of magnetic field from 3088 to 8468 gauss. The coefficients for the alloys were also examined over a range of temperature of about 5° C., but no change in the Hall coefficient was observed.

Two plates of pure antimony were examined, the crystals of one being very much larger than those of the other, due to the different methods of preparation. The Hall coefficient for the plate of large crystals was found to be 9 per cent. greater than that for the small crystals. It was constant for each plate for magnetic fields up to about 7000 gauss, but diminished for larger fields. The variation of the Hall coefficient with magnetic field for the plate of large crystals is shown in Table IV. and Graph V.

Heaps † found that the Hall coefficient for antimony diminished from +·220, corresponding to a magnetic field of 1700 gauss, to +·204, corresponding to a magnetic

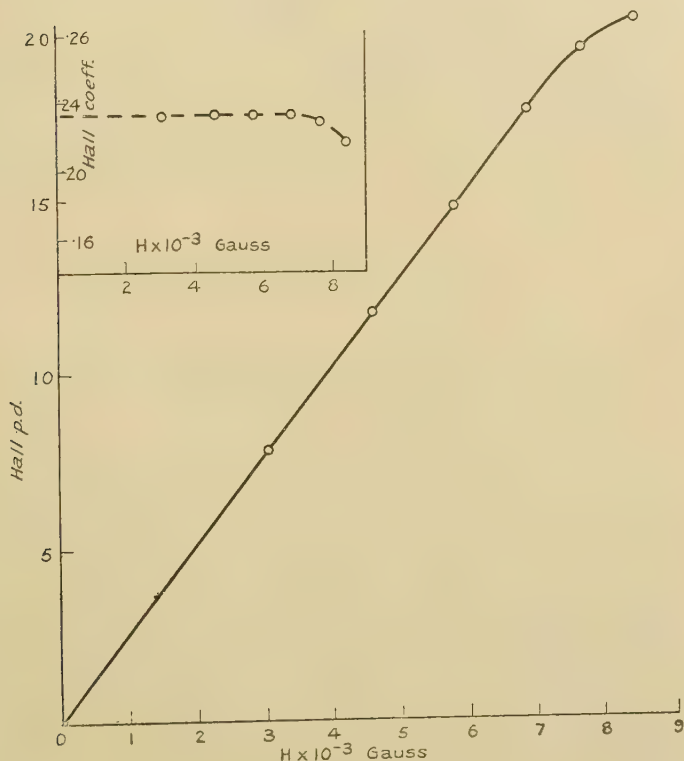
* Journ. Inst. Met. xxxvii. p. 29 (1927).

† Heaps, Phil. Mag. vol. I. Nov. 1925.

field of 3600 gauss, and that further increase in the magnetic field produced only a small diminution in the Hall coefficient.

The effect of annealing, as shown in Table I. and Graph I., was to produce a diminution in resistivity of all the alloys.

GRAPH V.



Summary.

(a) The Hall effect, electrical resistivity, temperature coefficient of resistance and thermoelectric power of the lead-antimony series of alloys have been determined. The alloys were chill cast, and the electrical resistivity at 0°C . was determined in this state. The resistivity was redetermined after the alloys had been annealed, and the annealing was continued until the resistivity showed no further variation. The temperature coefficient of resist-

ance, thermoelectric power, and Hall effect were then determined for the alloys in this final state.

(b) Each of the curves showing the relation between Hall effect, electrical resistivity, temperature coefficient of resistance, thermoelectric power, and the concentration of one metal in the alloy is continuous and no irregularities are obtained, but there is no indication of any close connexion between any of the phenomena.

(c) The effect of annealing was to produce a diminution in resistivity of all the alloys.

In conclusion, I wish to express my gratitude to Professor E. J. Evans, D.Sc., for his valuable help and advice.

December 1929.

LI. *The Behaviour of Electrons in Magnetic Fields.* By V. A. BAILEY, M.A., D.Phil.(Oxon.), F.Inst.P., Associate Professor of Physics, University of Sydney*.

1. THE best method for the determination of the drift-velocity W of electrons in gases in uniform electric fields is that originally used by J. S. Townsend and H. T. Tizard†, which depends on the principle that a uniform magnetic field, of intensity H and perpendicular to the electric field of intensity Z , deflects the stream of electrons through an angle θ , where $\tan \theta = HW/Z$.

It has been used with accuracy over a wide range of conditions in many kinds of gases, and has helped in obtaining definite information about the effects of collisions between electrons and molecules which has not been possible otherwise.

There are two effects which may, however, make its application difficult in certain circumstances, namely, the remarkable divergence of electronic streams in gases like argon and neon, and the formation of large numbers of negative ions in gases like hydrogen chloride, ammonia, nitric oxide, and nitrous oxide.

With the first it is possible to use large gas-pressures p and large electric intensities Z to reduce the divergence

* Communicated by Prof. J. S. Townsend, F.R.S.

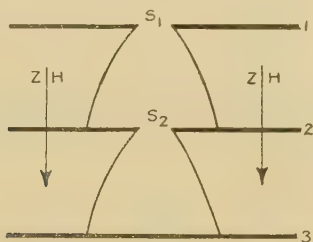
† J. S. Townsend, 'Motion of Electrons in Gases,' p. 21, or 'Electricity in Gases,' p. 121.

conveniently for a given value of Z/p ; but with the second even the use of small pressures and electric intensities may not always suffice to overcome the difficulties.

Another method for determining W has therefore been devised which provides a means of measuring the velocities of electrons in the presence of negative ions. It is not as simple as the one mentioned above, but it involves the same general principles.

The velocities for electrons in hydrogen obtained by the two methods are in good agreement, which is further evidence in support of these methods of investigation. The attack* on experiments of this kind (depending on statistical effects), made by the advocates of theories proposed by J. Franck, has no scientific foundation†.

Fig. 1.



2. Theoretical Principle.

The new method makes use of the reduction of the divergence of an electronic stream which occurs when a uniform magnetic field is applied in the same direction as the electric field, and is illustrated by the diagram in fig. 1.

When the stream issues from the slit S_1 the diffusion of the electrons causes it to diverge, which divergence is generally measured by means of the fraction R of the whole stream which passes through the second slit S_2 (or which arrives on a metallic strip) situated at a distance c . For given dimensions of the slits, and with no magnetic field, this fraction R can be expressed‡ as a known function $R(Z/kc)$ of the ratio Z/kc , where k is the mean energy of agitation of the electrons in terms of the mean energy of

* R. Atkinson, Proc. Roy. Soc. A, cxix. p. 335.

† J. S. Townsend, Proc. Roy. Soc. A, cxx. p. 511 (1928).

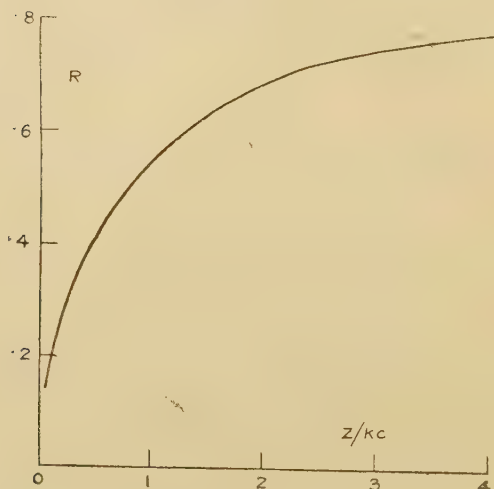
‡ Vide J. S. Townsend, 'Motion of Electrons in Gases,' pp. 7-9, and V. A. Bailey and J. D. McGee, Phil. Mag., Dec. 1928, p. 1076.

agitation of any molecule at 15° C. The fraction R is given in terms of the quantity Z/kc by the curve in fig. 2 when the slits are 4 mm. wide.

It will now be shown that the presence of the magnetic field reduces the divergence of the stream and affects the distribution ratio R as if the ratio Z/kc were replaced by $Z\sigma/kc$, where

$$\sigma = 1 + \left(\frac{HW}{Z} \right)^2 \dots \dots \dots (1)^*$$

Fig. 2.



The equations of motion † are

$$nu = -K_h \frac{\partial n}{\partial x},$$

$$nv = -K_h \frac{\partial n}{\partial y},$$

$$nw = -K \frac{\partial n}{\partial z} + nW,$$

* In e.m.u.

† J. S. Townsend, 'Electricity in Gases,' p. 101, where

$$\omega T = \frac{He}{m} T = \frac{HW}{Z}.$$

The y -axis is taken parallel to the slits, and the z -axis parallel to Z and H .

where n is the number of electrons per c. c. at a point (x, y, z) , nu, nv, nw are the net rates of flow of electrons across unit areas normal to the axes of coordinates, and K, K_h are the coefficients of diffusion of electrons respectively along and perpendicular to the magnetic field; these coefficients are related by the formula

$$K_h = K/\sigma.$$

The equation of continuity for the steady state is

$$\frac{\partial(nu)}{\partial x} + \frac{\partial(nv)}{\partial y} + \frac{\partial(nw)}{\partial z} = 0,$$

so, on eliminating nu, nv, nw by substitution from the equations of motion, the following is obtained:

$$\frac{1}{\sigma} \left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + \frac{\partial^2 n}{\partial z^2} = \frac{W}{K} \cdot \frac{\partial n}{\partial z}.$$

This can be simplified by integrating each term with respect to y , and taking as limits of integration points on the side-boundary, since in the actual instrument these points are too distant for any of the electrons to reach them, and so there

$$n = 0, \quad \frac{\partial n}{\partial y} = 0.$$

The result is

$$\frac{1}{\sigma} \frac{\partial^2 q}{\partial x^2} + \frac{\partial^2 q}{\partial z^2} = \frac{W}{K} \cdot \frac{\partial q}{\partial z},$$

where $q = \int n dy$ with the limits mentioned. On using Townsend's well-known relation

$$\frac{W}{K} = 41 \frac{Z}{k},$$

and making the substitution $z = c\zeta$, this in turn becomes

$$\frac{\partial^2 q}{\partial x^2} = 41 \left(\frac{Z\sigma}{kc} \right) \frac{\partial q}{\partial \zeta} - \frac{\sigma}{c^2} \frac{\partial^2 q}{\partial \zeta^2}. \quad \dots (2)^*$$

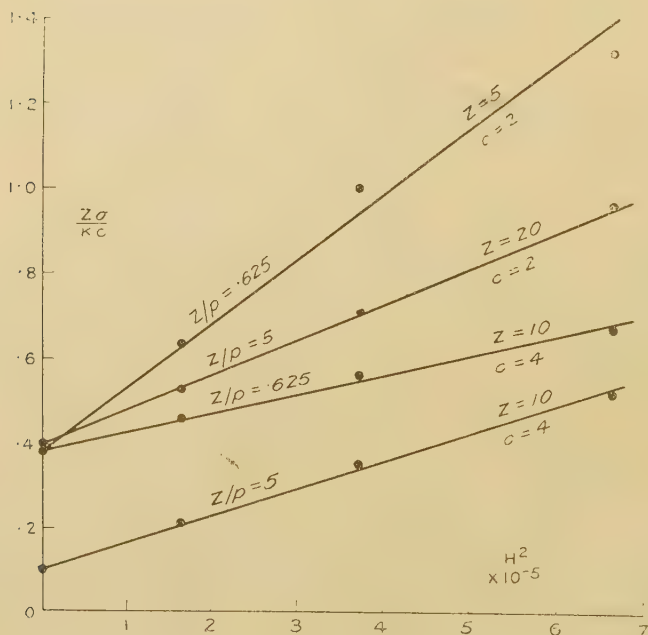
If the quantity Zc/k be not too small, the second term on the right may be neglected in comparison with the first, which gives

$$\frac{\partial^2 q}{\partial x^2} = 41 \left(\frac{Z\sigma}{kc} \right) \frac{\partial q}{\partial \zeta}.$$

* Z is in volts per centimetre.

Since ζ is a pure number with limiting values 0 and 1, and in the diffusion instrument only dimensions in the direction of the z -axis can be varied, the ratio R depends on the quantity $Z\sigma/kc$ alone; this quantity becomes Z/kc when the magnetic field is absent, so the assertion made about the divergence of an electronic stream in a magnetic field is now established*.

Fig. 3.



3. Experimental Verification.

Before considering the way in which this principle may be applied to the determination of the drift-velocity W , some experiments with hydrogen may be described which were made† with the purpose of testing its truth.

In each set of observations the pressure p , the electric intensity Z , and the spacing c of the slits were maintained constant, and the ratio R was determined for magnetic fields

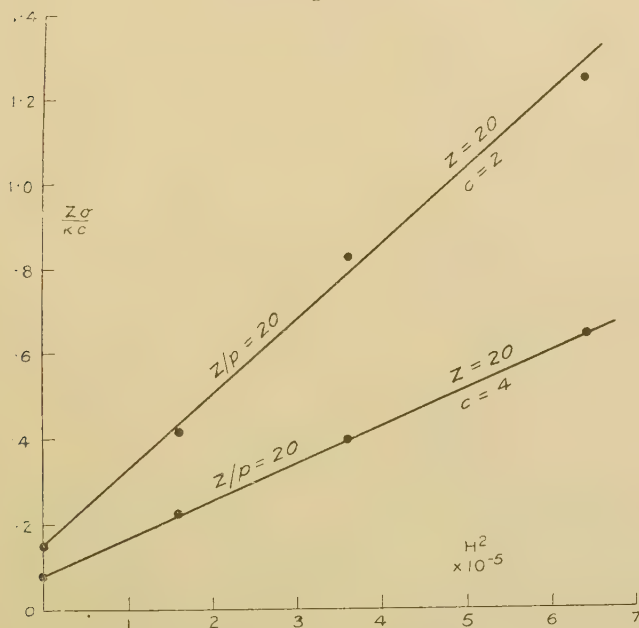
* A more rigorous, but less useful, statement is that the magnetic field affects the ratio R as if the dimensions of the instrument in the x -direction were increased by the factor $\sqrt{\sigma}$; this follows on making the substitution $x = \xi/\sqrt{\sigma}$ in the accurate differential equation.

† I am indebted to Mr. W. E. Duncanson, B.Sc., for most of them.

of different intensities. These intensities were 0, 408, 612, and 816 gauss. The values of $Z\sigma/kc$, corresponding to the values of R , were then obtained by means of the curve in fig. 2, and the points, with abscissæ $x=H^2$ and ordinates $y=Z\sigma/kc$, were plotted as in figs. 3 and 4.

Six sets of observations were thus made with the forces, pressures, and spacings given in the columns Z , p , and c of Table I. In each set the points (x, y) , corresponding to the four values of H , were found to lie on a straight line

Fig. 4.



(within limits of experimental error), as may be seen in the figs. 3 and 4*.

This is in agreement with the relation (1), for it may be written as

$$y = 10^{-16} \left(\frac{W^2}{Zkc} \right) x + \frac{Z}{kc},$$

and Z , c , k , and W are constants in each set of experiments.

Additional tests of the theory are provided by the slopes

* The points in fig. 4 correspond to the magnetic intensities 0, 400, 600, and 800.

dy/dx of the straight lines, for these enable the values of the velocity W to be calculated by means of the formula

$$W = \sqrt{Zkc \cdot dy/dx} \times 10^8,$$

and a comparison to be made with the values W_T obtained by means of Townsend's method.

This is shown in Table I., where Z is in volts/cm., p in mm. of mercury, c in centimetres, and W in centimetres/sec.

Thus the preliminary experiments give results in accordance with the theory, as is indicated by the agreement between the numbers in the last two columns.

TABLE I.

| Z/p . | Z . | p . | c . | $W \times 10^{-5}$. | $W_T \times 10^{-5}$. |
|---------|-------|-------|-------|----------------------|------------------------|
| .625 | 5 | 8 | 2 | 9.9 | 9.9 |
| | 10 | 16 | 4 | 10.9 | |
| 5 | 10 | 2 | 4 | 26 | 25.5 |
| | 20 | 4 | 2 | 29.5 | |
| 20 | 20 | 1 | 2 | 74.5 | 70 |
| | 20 | 1 | 4 | 74.5 | |

4. *Experimental Procedure.*

In practice the velocity W is more conveniently determined by means of the following method, which is based on the same principle, for, in general, with a given set of values of Z , p , and c , the value of k has to be determined as well as that of W . If, then, k be known, W is easily obtained by observing what value of H will make the divergence of the stream (measured by $R(Z\sigma/kc)$) identical with that of a stream composed entirely of negative ions (measured by $R(Z/c)$). For, if this value be denoted by H_0 , then

$$R\left(\frac{Z\sigma}{kc}\right) = R\left(\frac{Z}{c}\right).$$

Therefore $k = \sigma = 1 + (H_0 W/Z)^2$,

and so $W = \frac{Z}{H_0} \sqrt{k-1} \times 10^8$ (3)

from which W may be determined.

This method has been applied to hydrogen, with the results shown in Table II. The values of W in the fifth column have been calculated by means of equation (3), and are seen to agree well with the values W_T obtained by means of Townsend's method.

TABLE II.
 $c=4$ cm., $Z=4$ volts/cm., $R(Z/c)=.555$.

| Z/p . | k . | p . | H_0 . | $W \times 10^{-5}$. | $W_T \times 10^{-5}$. | $\frac{186 Z^2/H_0^2}{\times 10^4}$. | $\lambda \times 10^4$. |
|---------|-------|-------|---------|----------------------|------------------------|---------------------------------------|-------------------------|
| ·625 | 6·5 | 6·4 | 950 | 9·86 | 9·9 | | |
| 5 | 26 | ·8 | 760 | 26·3 | 25·5 | 51 | 46 |
| 20 | 78 | ·2 | 500 | 70·2 | 70 | 118 | 117 |

In connexion with this method it is interesting to observe that, by making the electrons appear to behave like negative ions, the effects of the latter (when present) on the divergence have been completely eliminated. It follows that, even when large numbers of negative ions are present, this method is still applicable, and so enables reliable values of W to be obtained when the values of k have been determined, as for example, in the recent work on Ammonia*.

A remarkable consequence of the method is that for values of k greater than 20 the values of λ , the fraction of its own energy lost by an electron in a collision, are given by the simple formula

$$\lambda = 186 Z^2/H_0^2, \quad (4)^\dagger$$

which involves only the electric and magnetic intensities. This follows from the relations

$$\lambda = 2·46 W^2/u^2, \quad u = 1·15 \sqrt{k} \times 10^7, \quad \text{and (3),}$$

where u is the velocity of agitation of an electron, when $1/k$ is negligible compared with unity, and is illustrated by the numbers in the last two columns of Table II.

Experiments for the determination of α/p , k , and W in ammonia and hydrogen chloride are now in progress, and the results will be published in the near future. These results will make possible reliable estimates of h , the probability of attachment of an electron which collides with a molecule.

* V. A. Bailey and J. D. McGee, *loc. cit.*

† Z is in volts/cm.

LII. *Hamilton's Principle and the Field Equations of Radiation.* By D. MEKSYN*.

§ 1. *Summary.*

THE problem of finding from Hamilton's Principle the most general field laws for an antisymmetric tensor of the second rank in five dimensions is solved.

The tensor has 10 (6 + 4) components four of which are complex, and two scalar functions are introduced as a result of the variational problem ; in all there are sixteen functions. The sixteen equations obtained are those of radiation.

For the case of free motion and, to the first approximation, for an external electromagnetic field these sixteen equations can be combined into eight (C. G. Darwin's equations)†. For the case of an electromagnetic field these equations are presented in a general tensor form, and the well-known operators

$$p_1 = \frac{h}{2\pi i} \frac{\partial}{\partial x} + \frac{e}{c} A_1 \dots$$

appear quite naturally as terms in contravariant differentiation.

It appears that the five-dimensional continuum represents a natural system of reference for radiation phenomena.

§ 2. *The Method of Solution.*

We have to solve the problem of finding the most general field equations for a particular tensor in space, which follow from Hamilton's Principle.

The method of solution is purely formal, and is equally well applied to 3, 4, and 5 dimensions.

We describe the field in all cases by an antisymmetric tensor of the second rank. For 3, 4, and 5 dimensions we obtain the electrostatic, electromagnetic, and the radiation field equations.

We solve the problem for an antisymmetric tensor of the second rank, because we know that for 3 and 4 dimensions this tensor represents some existing physical state, and, hence, it is natural to inquire whether this is also the case for 5 dimensions. The equations obtained represent a formal generalization of Maxwell's ones.

* Communicated by the Author.

† Proc. Roy. Soc. A, cxviii. p. 654.

In so far as the solution of the least action problem is concerned, we have to bear in mind the following: if the quantities in the Hamiltonian are differentials, the variational problem can be solved directly (as in dynamics), otherwise these quantities ought to be represented by means of differential coefficients of some other quantities, because without such representation the variational method cannot be applied.

Of course the equations obtained depend, to some extent, upon the form of this representation. We try therefore to find the most general form of representation of an anti-symmetric tensor of the second rank, with the only limitations that these expressions must not conflict with the law of transformation of the particular space.

§ 3. Application to Three Dimensions.

In order to make these considerations clear we give here the solution of this problem for the case of three dimensions.

The field is described by a three-vector $E(E_x, E_y, E_z)$. The Hamiltonian is

$$W = \frac{1}{2} \int E^2 dx dy dz. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now Stokes has proved* that a three-vector can be represented by means of scalar and vector potentials ϕ , $V(V_x, V_y, V_z)$ as follows:—

$$E = \text{grad } \phi + \text{rot } V, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

under the condition that

$$\text{div } V = 0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As a matter of fact ϕ and V are found from

$$\nabla^2 \phi = \text{div } E; \quad \nabla^2 V = -\text{rot } E.$$

The field equations are obtained from $\delta W = 0$, using (2) and (3).

We have

$$\int \left(\delta \frac{E^2}{2} + \mu \delta \text{div } V \right) dx dy dz = 0. \quad . \quad . \quad . \quad (4)$$

Using (2), and integrating by parts, we easily find that (4) is equivalent to

$$-\int \{ \text{div } E \cdot \delta \phi + ([\text{grad } \mu - \text{rot } E] \cdot \delta V) \} dx dy dz = 0,$$

* A. E. H. Love, 'A Treatise on the Mathematical Theory of Elasticity,' p. 47 (1920).

and the field equations are

$$\left. \begin{aligned} \operatorname{div} \mathbf{E} &= 0, \\ \operatorname{rot} \mathbf{E} &= \operatorname{grad} \mu. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It can be shown that all four quantities \mathbf{E} and μ satisfy Laplace's equation.

In (5) there appear, except for the electrostatic vector \mathbf{E} , also a new quantity μ . It will be shown in a separate paper that this quantity represents the potential of a hydrostatic pressure, which is necessary for stability of an electron.

§ 4. *Some Metrical Properties of Five-dimensional Space.*

We give here for convenience' sake a few well-known laws of the five-dimensional space*.

The transformations for the space-time coordinates do not depend upon the fifth dimension, and are the same as in the theory of Relativity. The transformation of the fifth dimension is merely

$$x_5' = x_5. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If we apply these rules to an antisymmetric tensor of the second rank

$$T^{\nu\mu\lambda} = \frac{\partial x_{\mu}'}{\partial x_{\alpha}} \frac{\partial x_{\nu}'}{\partial x_{\beta}} T^{\alpha\beta}, \quad . \quad . \quad . \quad . \quad (7)$$

we find that the six space-time components are transformed as an antisymmetric tensor of the second rank in the Theory of Relativity, and the four components associated with the fifth dimension

$$T^{\nu\mu 5} = \frac{\partial x_{\mu}'}{\partial x_{\alpha}} \frac{\partial x_5'}{\partial x_{\beta}} T^{\alpha\beta} = \frac{\partial x_{\mu}'}{\partial x_{\alpha}} T^{\alpha 5} \quad . \quad . \quad . \quad (8)$$

are transformed as a four-vector.

The fundamental tensor is

$$\left. \begin{aligned} \gamma^{ik} &= g^{ik}, & \gamma^{i5} &= -\beta\phi^i, & \gamma^{55} &= 1 + \beta^2\phi_i\phi^i, \\ \gamma_{ik} &= g_{ik} + \beta^2\phi_i\phi_k, & \gamma_{i5} &= \beta\phi_i, & \gamma_{55} &= 1 \end{aligned} \right\} \quad (i, k = 1, 2, 3, 4), \quad (9)$$

where g_{ik} is the gravitational tensor and ϕ_i is the vector-potential of an external electromagnetic field.

* O. Klein, *Zeits. f. Phys.* xlv. p. 189 (1928).

For β we take the value

$$\beta = \frac{e}{imc^2}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

For this value of β the track of an electron becomes, as Fock* and Fisher have shown, a null geodesic, and Schrödinger's wave equation appears to be the usual wave equation in this space.

§ 5. *Representation of an Antisymmetric Tensor of the Second Rank by means of Two Vectors.*

The method of derivation of the field equations in the case of five dimensions is similar to the classical one, and is based upon representation of an antisymmetric tensor of the second rank by means of differential coefficients of two five-vectors. As we have pointed out, such representation is necessary in order to solve the variational problem.

Let us find out under what conditions this is possible.

Let $F_{\alpha\beta}$ be an antisymmetric tensor, $k_1 \dots k_5$ and $l_1 \dots l_5$ two five-vectors. $F_{\alpha\beta}$ can be expressed as follows:—

$$F_{\alpha\beta} = \frac{\partial k_\alpha}{\partial x_\beta} - \frac{\partial k_\beta}{\partial x_\alpha} + \frac{\partial l_\delta}{\partial x_\gamma} - \frac{\partial l_\gamma}{\partial x_\delta}, \quad . \quad . \quad . \quad (11)$$

$$\alpha\beta\gamma\delta = (1, 2, 3, 4).$$

The signs in the six equations (11) correspond to an odd number of permutations in the series $\alpha\beta\gamma\delta$. Also

$$F_{\alpha 5} = \frac{\partial k_\alpha}{\partial x_5} - \frac{\partial k_5}{\partial x_\alpha}; \quad G_{\alpha 5} = \frac{\partial l_\alpha}{\partial x_5} - \frac{\partial l_5}{\partial x_\alpha}, \quad . \quad (11a)$$

$$\alpha = (1, 2, 3, 4).$$

It appears that, except for $F_{\alpha\beta}$, new quantities $G_{15} \dots G_{45}$ have to be introduced; we can thus consider the fifth dimensional components of $F_{\alpha\beta}$ as complex.

The origin of these quantities is as follows:—In order to justify our form of representation of the tensor $F_{\alpha\beta}$ by means of two vectors k and l , we have to prove that from a given tensor $F_{\alpha\beta}$ we can always discover the vectors k, l (see equations (12)).

In the case of 3 and 4 dimensions k and l satisfy the usual wave equation, and we may expect that this will hold good for the present case.

* *Zeits. f. Phys.* xxxix, p. 22 (1926); J. K. Fisher, *Proc. Roy. Soc. A*, cxxiii, p. 489 (1929).

From the simple algebra of evaluating the equations (12) it follows that, unless we make use of additional quantities $G_{15}\dots$, we are unable to obtain the required equations for k and l .

We have now to prove that if $F_{\alpha\beta}$ and $G_{15}\dots$ are given, the two vectors k and l can be found.

The following expressions are easily obtained :—

$$\left. \begin{aligned} \frac{\partial F_{\alpha\beta}}{\partial x_\gamma} + \frac{\partial F_{\beta\gamma}}{\partial x_\alpha} + \frac{\partial F_{\gamma\alpha}}{\partial x_\beta} + \frac{\partial G_{\delta\delta}}{\partial x_\delta} &= \bigwedge^2 l_\delta - \frac{\partial L}{\partial x_\delta}, \\ \frac{\partial G_{\alpha\delta}}{\partial x_\alpha} &= -\bigwedge^2 l_5 + \frac{\partial L}{\partial x_5}, \\ \alpha\beta\gamma\delta &= (1, 2, 3, 4). \end{aligned} \right\} \quad (12)$$

The law of composition of the four equations which follow from the first expression in (12) is simple ; the values α, β, γ are any three from 1, 2, 3, 4 taken in order ; the sign in (12) corresponding to an even number of permutations in the series $\alpha\beta\gamma\delta$. Also

$$\begin{aligned} \frac{\partial F_{\alpha\beta}}{\partial x_\beta} &= \bigwedge^2 k_\alpha - \frac{\partial K}{\partial x_\alpha}, \quad . \quad . \quad . \quad (12a) \\ \alpha, \beta &= 1, 2, 3, 4, 5. \end{aligned}$$

In all the equations the expression must be summed with respect to those indices which occur twice.

In the equations (12) and (12a)

$$\left. \begin{aligned} K &= \text{div } k, \\ L &= \text{div } l, \\ \bigwedge^2 &= \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial x_4^2} + \frac{\partial^2}{\partial x_5^2}. \end{aligned} \right\} \quad (13)$$

We assume

$$K=0, \quad L=0, \quad . \quad . \quad . \quad (14)$$

and the two vectors $k_1\dots k_5, l_1\dots l_5$ can be evaluated from (12) and (12a).

It is clear that not all components of the tensors F and G are independent; the two antisymmetric tensors have fourteen components, whereas we have only eight independent quantities to express them. Hence the components of the antisymmetric tensor must satisfy six additional conditions. They are easily found, and are given later (equations (19)).

§ 6. *The Variational Problem and the Field Equations.*

The Hamiltonian has in this case the following expression:—

$$W = \frac{1}{2} \int (F_{14}^2 + F_{24}^2 + F_{34}^2 + F_{23}^2 + F_{31}^2 + F_{12}^2 + F_{15}^2 + F_{25}^2 + F_{35}^2 + F_{45}^2 + G_{15}^2 + G_{25}^2 + G_{35}^2 + G_{45}^2) dx_1 dx_2 dx_3 dx_4 dx_5. \quad (15)$$

The field equations are obtained from the condition

$$\delta W = 0. \quad (16)$$

In the evaluation of (16) we have to make use of the equations (11), (11*a*), and (14) after the latter have been multiplied by indeterminate factors μ and λ respectively; the Hamiltonian becomes

$$\int \delta \left(\frac{F_{14}^2 + \dots + G_{45}^2}{2} \right) + \mu \delta K + \lambda \delta L) dx_1 \dots dx_5 = 0. \quad (16a)$$

Integrating by parts (16*a*) we easily find the required equations. They are as follows:—

$$\frac{\partial F^{\alpha\beta}}{\partial x_\beta} + \frac{\partial \mu}{\partial x_\alpha} = 0, \quad (17)$$

$$\alpha, \beta = 1, 2, 3, 4, 5;$$

also

$$\left. \begin{aligned} \frac{\partial F^{\alpha\beta}}{\partial x_\gamma} + \frac{\partial F^{\beta\gamma}}{\partial x_\alpha} + \frac{\partial F^{\gamma\alpha}}{\partial x_\beta} + \frac{\partial G^{\delta 5}}{\partial x_5} + \frac{\partial \lambda}{\partial x_\delta} &= 0, \\ \alpha\beta\gamma\delta &= (1, 2, 3, 4), \\ \frac{\partial G^{5i}}{\partial x_i} + \frac{\partial \lambda}{\partial x_5} &= 0, \quad i = 1, 2, 3, 4, 5. \end{aligned} \right\} \quad (18)$$

The first expression in (18) comprises four equations; the signs correspond to an even number of permutations in the series $\alpha\beta\gamma\delta$.

As we have pointed out, there are six additional conditions to be imposed upon the components of the antisymmetric tensor. It is easily verified from (11) and (11*a*) that these conditions are

$$\frac{\partial F_{\alpha 5}}{\partial x_\beta} - \frac{\partial F_{\beta 5}}{\partial x_\alpha} + \frac{\partial F_{\delta 5}}{\partial x_\gamma} - \frac{\partial F_{\gamma 5}}{\partial x_\delta} - \frac{\partial F_{\alpha\beta}}{\partial x_5} = 0, \quad (19)$$

$$\alpha, \beta, \gamma, \delta = (1, 2, 3, 4).$$

These are six equations, and the signs in (19) correspond to an odd number of permutations in the series $\alpha\beta\gamma\delta$.

In order to eliminate imaginary quantities from the equations (17–19), and bring them into the same form as

Maxwell's equations, we have merely to bear in mind that the following quantities are purely imaginary :—

$$x_4, F_{15}, F_{25}, F_{35}, G_{45}, F_{12}, F_{31}, F_{23}, \mu. \dots (20)$$

The equations obtained (17–19) can be easily brought into J. M. Whittaker's equations * ; his six-vector and two four-vectors correspond to our antisymmetric tensor with fourteen components. Whittaker's way of deriving these equations is different from ours. He assumes eight equations, as given, and derives the other eight ones from Hamilton's principle.

§ 7. We show now that the system of sixteen equations (17–19) can be easily brought into C. G. Darwin's form of Dirac's equations.

We consider the case when there is no electromagnetic or gravitational field. For that case we need not distinguish between covariant and contravariant tensors.

We combine the first three equations of (17) with (19) (for F_{14}, F_{24}, F_{34}) multiplied by $i = \sqrt{-1}$ respectively, and combine the fourth with the fifth equations (17) multiplied also by i ; the same procedure we adopt with respect to equations (18) and (19) (for F_{23}, F_{13}, F_{12}). The result is

$$\left. \begin{aligned} & \left(\frac{\partial}{\partial x_4} + i \frac{\partial}{\partial x_5} \right) (F_{14} - iF_{15}) + \frac{\partial}{\partial x_2} (F_{12} - iG_{35}) \\ & \quad - \frac{\partial}{\partial x_3} (F_{31} - iG_{25}) + \frac{\partial}{\partial x_1} (\mu + iF_{45}) = 0, \\ & \left(\frac{\partial}{\partial x_4} + i \frac{\partial}{\partial x_5} \right) (F_{24} - iF_{25}) - \frac{\partial}{\partial x_1} (F_{12} - iG_{35}) \\ & \quad + \frac{\partial}{\partial x_3} (F_{23} - iG_{15}) + \frac{\partial}{\partial x_2} (\mu + iF_{45}) = 0, \\ & \left(\frac{\partial}{\partial x_4} + i \frac{\partial}{\partial x_5} \right) (F_{34} - iF_{35}) + \frac{\partial}{\partial x_1} (F_{31} - iG_{25}) \\ & \quad - \frac{\partial}{\partial x_2} (F_{23} - iG_{15}) + \frac{\partial}{\partial x_2} (\mu + iF_{45}) = 0, \\ & \left(\frac{\partial}{\partial x_4} - i \frac{\partial}{\partial x_5} \right) (\mu + iF_{45}) - \frac{\partial}{\partial x_1} (F_{14} - iF_{15}) \\ & \quad - \frac{\partial}{\partial x_2} (F_{24} - iF_{25}) - \frac{\partial}{\partial x_3} (F_{34} - iF_{35}) = 0. \end{aligned} \right\} \dots (21)$$

These are exactly Dirac's equations in Darwin's form.

* Proc. Roy. Soc. A, cxxi. p. 543.

To obtain the terms mc we have merely to suppose that the fifth coordinate enters in the functions in the following dependence :—

$$e^{\frac{2\pi i}{h} m c x_5} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (22)$$

§ 8. The Field Equations for an External Electromagnetic Field.

To determine the field equations for the case of an external electromagnetic field we have to represent our equations in general tensor form *.

The equations (17) are easily written out in a tensor form. They are

$$F^{a\beta}{}_{\beta} + \mu^a = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$\alpha, \beta = (1-5),$$

where μ^a represents a contravariant differentiation with respect to x^a , or

$$\mu^\alpha = \gamma^{\alpha\sigma} \mu_\sigma. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We transform in (23) the terms F^{a5}_5 . We have, for instance,

$$F^{15} = \gamma^{1\alpha} \gamma^{5\beta} F_{\alpha\beta} = \gamma^{11} \gamma^{52} F_{12} + \gamma^{11} \gamma^{53} F_{13} + \gamma^{11} \gamma^{54} F_{14} + \gamma^{11} \gamma^{55} F_{15} \\ + \gamma^{15} \gamma^{15} F_{51} + \gamma^{15} \gamma^{52} F_{52} + \gamma^{15} \gamma^{53} F_{53} + \gamma^{15} \gamma^{54} F_{54}. \quad (25)$$

If we insert in (25) the values (9) of the fundamental tensor for the case when there is no gravitation, we easily find

$$F^{15} = F_{15} + \gamma^{52} F^{12} + \gamma^{53} F^{13} + \gamma^{54} F^{14}, \quad . \quad . \quad (26)$$

and hence the first equation (23) takes the form

$$F^{12}_2 + \gamma^{52} F^{12}_5 + F^{13}_3 + \gamma^{53} F^{13}_5 + F^{14}_4 + \gamma^{54} F^{14}_5 + F_{15,5} + \mu^1 = 0,$$

or finally the first set of equations (23) becomes

$$\left. \begin{aligned} F^{12,2} + F^{13,3} + F^{14,4} + F_{15,5} + \mu^1 &= 0, \\ . &. \\ F^{41,1} + F^{42,2} + F^{43,3} + F_{45,5} + \mu^4 &= 0, \\ F_{51}{}^1 + F_{52}{}^2 + F_{53}{}^3 + F_{54}{}^4 + \mu_5 &= 0. \end{aligned} \right\} \cdot \quad (27)$$

* H. T. Flint, Proc. Roy. Soc. A, cxxiv. p. 143.

These appear to be equations between quantities not of the same variance, but it is to be noted that this results from the removal of the gravitational field so that there is no distinction between the two types of variance.

We have to bear in mind that a contravariant differentiation with respect to $x_k (k=1, 2, 3, 4)$ is, to the first approximation, equivalent to the operator $\frac{h}{2\pi i} \cdot \frac{\partial}{\partial x_k} + \frac{e}{c} \phi_k$.

We see that this operator appears quite naturally in our equations.

To present (18) in a tensor form we make use of the same procedure as in the case of the second set of Maxwell's equations in the Special Theory of Relativity. We introduce, instead of the tensor $F^{\alpha\beta}$, a new one in the following manner:—

$$\left. \begin{array}{l} \text{Instead of } F^{43}, F^{24}, F^{32}, F^{41}, F^{13}, F^{21}, \\ \text{we take } G^{12}, G^{13}, G^{14}, G^{23}, G^{24}, G^{34}. \end{array} \right\} \quad (28)$$

We complete thus the missing terms of the tensor $G^{\alpha\beta}$. To find the covariant components of G^{ik} we make use of the six equations

$$\gamma^{4\alpha} \gamma^{3\beta} F_{\alpha\beta} = \gamma^{1\alpha} \gamma^{2\beta} G_{\alpha\beta}, \quad . \quad . \quad . \quad (29)$$

$$. \quad . \quad . \quad . \quad . \quad .$$

and four equations

$$G^{i5} = \gamma^{i\alpha} \gamma^{5\beta} G_{\alpha\beta}. \quad . \quad . \quad . \quad . \quad (30)$$

From (29) and (30) we easily find the covariant tensor $G_{\alpha\beta}$. So, for instance,

$$G^{15} = \dot{G}_{15} + \gamma^{52} F_{43} + \gamma^{53} F_{24} + \gamma^{54} F_{32}.$$

Now the equations (18) become

$$\begin{aligned} G^{\alpha\beta} + \lambda^\alpha &= 0, \quad . \quad . \quad . \quad . \quad (31) \\ \alpha, \beta &= (1-5), \end{aligned}$$

and the five equations (31) can be represented in the same form as (27).

We transform the set of equations (19). The simplest assumption would be for the first equation (19)

$$F_{15,2} - F_{25,1} + G_{45,3} - G_{35,4} - F_{12,5} = 0. \quad . \quad (32)$$

If we express F_{12} by means of F^{12} , when the gravitational field is absent,

$$F^{12} = F_{12} + \gamma^{15} F_{52} + \gamma^{25} F_{15},$$

and combining this expression with (32), we obtain

$$F_{15}^2 - F_{25}^1 + G_{45,3} - G_{35,4} - F_{5}^{12} = 0,$$

or the equations are not symmetric with respect to the functions G_{k5} and F_{i5} ; they do not agree to the first approximation with Dirac's equations.

We assume, therefore, the following form for our equations:—

$$(F^{\alpha}_{\ 5})^{\beta} - (F^{\beta}_{\ 5})^{\alpha} + (G^{\delta}_{\ 5})^{\gamma} - (G^{\gamma}_{\ 5})^{\delta} - F^{\alpha\beta}_{\ 5} = 0, \quad (33)$$

$$\alpha, \beta, \gamma, \delta = (1, 2, 3, 4).$$

The signs in the six equations (33) correspond to an odd number of permutations in the series $\alpha\beta\gamma\delta$. Here $(F^{\alpha}_{\ \beta})^{\gamma}$ means the contravariant differentiation of $F^{\alpha}_{\ \beta}$ with respect to x_{γ} .

For the case when there is no gravitation

$$F^1_{\ 5} = \gamma^{1\alpha} F_{\alpha 5} = F_{15},$$

or the operators are performed upon the same functions as in (27) and (31).

The field equations for the general case of an electromagnetic and gravitational force are (23), (28), (31), and (33).

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LIII. *Frictional Electricity.* By Professor P. E. SHAW,
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THIS subject is far the oldest branch of electricity, and it provides far the easiest way of raising electric charges. There can be no easier experiment than that of rubbing one's fountain-pen on a coat-sleeve and using the excited pen to raise a small scrap of paper.

It is all the more remarkable that, after a century of great advance in the theory and application of electricity, and after a generation of unparalleled progress in its fundamentals, our knowledge of frictional (or tribo-) electricity is still meagre. Writers of text-books and

* Communicated by the Author.

reference books allot a mere page or two of qualitative information, and then, after brief and guarded statements on the subject, seem glad to leave it for safer and more matured topics, such as, say, voltaic or thermo-electricity. However, it is possible after the progress made in tribo-electricity in the last fifteen years to bring together many new salient facts. Closer study of this subject, so simple-seeming, has revealed complications apparently unsuspected by the earlier workers. We will indicate some experimental results and some principles which are only found in recent research, or are revealed now for the first time.

I.—The time-honoured method of discharging an excited body is to pass it through a flame. This process is unnecessarily drastic ; for the ionized zone above and around a flame acts quite well. But the flame method is definitely bad, since it not only discharges the body but may, as we shall see in the next section, modify its surface profoundly. How often has a teacher, using the flame method, found his experiment go all wrong, and then had to take refuge in the traditional excuse that frictional electricity is a fickle, “fortuitous” subject on account of atmospheric moisture ! To discharge a rod we do not use the flame method, but its surrounding zone.

II.—When a glass rod which rubs *positive* to silk is placed, even for a second or two, in a flame, it is then found to rub *negative* to the silk, and, further, the friction between the glass and silk has now increased considerably. But on continuing the rubbing with vigour the glass returns to its positive state, and friction is again low. This reversible process, which is quite dependable, was investigated by the writer* ; but its physical significance has only just been revealed. We can rub glass from the negative to the positive state by ordinary silk, flannel, or felt ; but when these fabrics have been exhaustively cleansed of fats, waxes, etc. by purest benzene or chloroform, the glass is persistently negative. Now, if on the cleansed fabric any one of many solid organic compounds of low melting-point be placed, the glass will after persistent rubbing become positive. The choice of organic material is very great ; fatty, bibasic, or aromatic acids, esters or

* Shaw, Proc. Phys. Soc., April 1915 ; Proc. Roy. Soc. A, xciv. (1917).

ketones, all operate well. It is clear, then, that an organic film, with good polish, is formed on the glass and is removed at once by a flame, or, alternatively, by raising its temperature to 300°C . Thus in the well-known experiment of rubbing glass positive with silk, the surface rubbed is not glass at all, but an organic film; but when clean fabric is rubbed on clean glass the charge on the latter is invariably negative. Sir W. B. Hardy* in his investigations on boundary lubrication, found such films to have very low friction, and to be very tenacious. He considered them very thin, possibly monomolecular.

Recent work has shown that these organic films form more or less readily not only on glass but on various metals, ebonite, etc., and as with glass, and by their presence, change these surfaces from a negative to a positive one when rubbed with, say, filter paper or clean silk.

III.—Faraday and others have observed that apparently identical solids, say two like feathers, become charged when rubbed together. This effect has now been investigated †. Excellent material for the purpose is ebonite. Two pieces of it cut from the same rod and rubbed will, in general, give charges of an irregular kind. To make these charges regular anneal the rods by raising them to 100° in boiling water. Dry them and allow to cool. Then, laying one rod (*a*) across the other (*b*), stroke the latter with the former. At once (*a*) becomes negative, (*b*) positive. This electric separation is not due to any difference in the rods, for when the rods are changed, so that (*b*) is rubbed on (*a*), (*b*) becomes negative and (*a*) positive. On continuing the rubbing of (*b*) on (*a*) the charges gradually decrease, vanish, and finally reverse signs, so that (*b*) is now positive.

These effects are attributable to the different strains arising on the rods where they rub one another. The two surfaces being equally hard must both become strained in rubbing. But the upper rod (*b*) bears throughout a stroke on one spot, so that at that spot the effect is concentrated, and the strain grows quickly; the other rod (*a*) is rubbed along a whole generating line, so the strain is distributed over a large area, and no part of it becomes greatly strained until after many strokes.

* Proc. Roy. Soc. A, cviii. (1925).

† Shaw, Proc. Phys. Soc., August 1927.

The upshot is that the acting parts of (*b*) and (*a*), being strained in different degree, the rods, though *chemically* identical, differ *physically*. They therefore act triboelectrically as different bodies, and become charged negative and positive respectively.

To pursue the argument : since the energy spent on each rod is the same, the smaller area of (*b*) becomes hotter than the larger area of (*a*), and being hotter recovers more quickly from the strain. So in the end the strain on (*a*) becomes greater than that on (*b*), and the sign of the charge reverses, as we have seen. The rule is that the more strained surface is negative to the less strained. Other materials, *e. g.*, amberite, celluloid, and metals, show the same effects. It has been observed by Beilby * that two wires of identical metal, one strained, the other annealed, show the thermo-electric effect when placed in contact. Thus we have independent support for the statement that strain changes the physical nature of a surface.

IV.—Rubbing is the usual way of exciting charges, but normal impact of the two surfaces serves quite well, as shown by Richards † and by others. On consideration one sees that in normal impact, while most of the force is expended in direct compression of the two surfaces, these will in general experience a certain amount of tangential or sliding movement, the only purely normal contact occurring in the ideal case when two perfectly plane surfaces meet, in normal contact.

Thus the word “frictional” in its usual sense is not strictly applicable to this subject, since triboelectricity arises without rubbing or friction.

An interesting effect occurs in this connexion. Let two rods of ebonite or other good insulator be struck together violently with a glancing blow so as to meet in oblique, not normal, impact. If the two rods be then together brought near a gold-leaf electroscope there will generally be found on them a net *negative* charge of considerable amount. Faraday’s law states that the charges on the two surfaces produced by rubbing are equal and opposite, *i. e.*, the net charge is nil. This is true for *rubbing* where the surfaces

* Beilby, ‘Aggregation and Flow of Solids,’ Macmillan & Co.

† Richards, Phys. Rev. 1920, p, 290.

remain in contact for much longer time than in the process of oblique *impact*. But the law fails, as we see, for violent oblique impact. We have failed to find it in cases of normal impact. In the case of a glancing blow the surfaces separate more quickly.

In the circumstances we cannot conceive that negative electricity is generated by the impact; so the only conclusion is that one or both of the rods has lost some *positive* charge to the air. To explain this one supposes that something like an explosion occurs on one or both of the surfaces, the ejectamenta to the surrounding air having net positive charge. We know from Hertz's theory of elastic deformation that the force per unit area at the centre of the contact area in impact may amount to many thousands of atmospheres, and when the two surfaces recoil after the blow is delivered some material may be shot out of the surfaces. If the positive surface loses more than the negative one, the above effect would be produced.

V.—The results of an impact experiment of a different kind lends support to the principle just enunciated. Rudge* showed that certain powders, when blown from a vessel by a blast of air, attain charges. The writer† has investigated this effect with sand blown through a sand-tube and with a variety of metal filings blown through metal tubes. In each case the filings and tube are of the same material, so there is similarity between this case and the impact of two like insulators, as in the last section. The charge is measured for filings, tube, and emerging air, and the result for all the cases tried is that the filings, the tube, and the air each attain charges which, within experimental errors, are regular. So here again oblique impact between like materials gives rise to a net charge for the two solid materials used and an equal and opposite net charge for the air. It may be observed in passing that this affords an explanation of several meteorological phenomena, such as lightning discharges in volcanic eruptions, electrical sand-storms in deserts, and electrical snow-storms sometimes observed in the Antarctic.

* Rudge, Roy. Soc. Proc. A, May 1914.

† Shaw, Roy. Soc. Proc. A, cxxii. (1929).

VI.—We have seen in Section II. that organic films on a surface profoundly affect its triboelectric behaviour. There are three other kinds of film * which have a definite influence on results :—(1) Adsorbed water films condense from the air on many surfaces, particularly glass ; these act in a negative way. (2) alkaline films or surfaces also act negatively due to the formation when rubbed of $-(OH)$ ions. (3) acid films act positively, on account of the production of $+(H)$ ions. These effects, which are pitfalls for the unwary, demonstrate the futility of seeking data from solids of uncertain composition or surface purity. Many acids and alkalies are extraordinarily tenacious on neutral surfaces like glass ; so that, after they have been applied to a surface, abrasion by a hard solid is the only way to move their residual films.

VII. A comprehensive theory to embrace all the known effects of triboelectricity cannot be produced till the subject has been more fully investigated quantitatively. Many physicists have been content to borrow the Volta contact potential principle, so well established for metals, to explain the charges arising triboelectrically when surfaces, whether of metals or non-metals, rub together. Now, we have seen that film effects may play a large part in the nature of triboelectric charges, and allowance for these films must be most carefully made.

But even allowing that such films are adventitious, and should be removed before the real triboelectric effects are observed, we still have to reckon with two factors other than a mere contact effect. These only come into being because of the relative *motion* of the surfaces, and therefore cannot arise in the Volta contact potential, which is purely a statical phenomenon.

These two factors are (1) strain of surfaces, and (2) rise of temperature, both caused by the rubbing ; and we have seen that results are fundamentally affected by them.

Riecke † and others ‡ have established formulae for the charge arising when two insulators are rubbed together. In the equation

$$Q = \frac{a}{b} (1 - e^{-bw}),$$

* Shaw & Jex, Roy. Soc. Proc. A, cxviii. (1928).

† Wied. Ann. 1787, p. 414.

‡ French, Phys. Rev., Feb. 1917.

Q = charge attained, w = total work done, a , b are constants for the surfaces depending on their specific excitability and leakage. But such simple expressions take no account of the two dynamical factors mentioned above.

Another fundamental objection to a simple volta contact theory is that, whereas in this theory the potential difference arises when the metals are in contact, in triboelectricity the charge is only seen after separation. Some experiments have been made to demonstrate that charges really do exist between insulators when in contact, but they seem most inconclusive. Even if they are allowed to stand as proof on the point, it must be remembered that in triboelectricity the charges are invariably observed *after the surfaces separate*. Is it to be assumed that the process of separating linked molecules does not of itself cause charging?

It will surely be difficult, or impossible, to appraise the influence of these two dynamical factors, so that the charges can be calculated when any given pure substances of known figure are rubbed together with a known expenditure of work. The utmost attainable outcome may be an empirical equation, which, of course, is always a formulated confession of ignorance.

There is a large and promising field of research in this subject. Triboelectricity, which deals with the rough clash of solid surfaces, proves to be a very involved subject. Solid surfaces are more complex than are liquid surfaces, but in recent years much light has been shed on their composition by many different lines of reasoning, notably: the theory of the lattice electrical structure of crystals: the Debye theory of the dipole nature of dielectric molecules: the double electric layer of Helmholtz: Hardy's theory of boundary lubrication: and the Langmuir-Adam work on the monomolecular solid films on water.

The theory of the polar structure of atoms and molecules, and their resultant orientation in suitable fields, should prove as powerful in triboelectricity as in other fields of research.

LIV. *On new Methods in Statistical Mechanics.* By MEGHNAD SAHA, D.Sc., F.R.S., and RAMESH CHANDRA MAJUMDAR, M.Sc., Allahabad University*.

AT the present time a number of new methods are being developed in statistical mechanics, and it is difficult to see the connexion amongst them. In this essay an attempt is made to review these methods and supply the link amongst the different theories.

Almost all the old (Planck) and new methods (Bose-Einstein ⁽¹⁾, Fermi-Dirac ⁽²⁾) start with Boltzmann's theorem

$$S = k \log W,$$

and with Planck's definition of W , viz. :—

W = Thermodynamical Probability.

There is an alternative function G due to Boltzmann ⁽³⁾ and Gibbs ⁽⁴⁾ which may be described as the total phase volume described by a thermodynamical system. Ehrenfest and Trkal ⁽⁵⁾ treat problems of chemical equilibrium etc. with the aid of this function (they called it $\{\gamma\}$), and find their method superior to Planck's. There is a certain amount of ambiguity in Planck's definition of W ; according to him W is a whole number, but Ehrenfest and Trkal have shown that Planck's expression for W has to be divided by $N!$ to get the correct expression for S . The need for this operation is not clear. Planck ⁽⁶⁾ has apparently admitted the soundness of this criticism, and in a recent paper puts a new interpretation on W . He defines W as the maximum number of probable states which can give rise to the total energy E . Planck shows that, with this definition,

$$W = \frac{G}{h^{3N} N!} \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

The same conclusion has been reached independently and simultaneously by Saha and Sur ⁽⁷⁾ from different conceptions. They emphasize the necessity for laying down a unit of probability. At absolute zero $S = 0$ and $W = 1$, and the total phase-volume described = $h^{3N} N!$ in the simplest case (*i. e.*, a perfect monatomic gas). Denoting this by G_0 , and the corresponding probability by unity, the mathematical value of probability at any temperature

$$W = \frac{G}{G_0} = \frac{G}{h^{3N} N!}.$$

* Communicated by the Authors.

The conceptions of Planck and Saha and Sur, though apparently different, are in essence identical.

We shall therefore start with the theorem (1) and calculate W , introducing (1) classical conceptions, (2) the Fermi-Dirac condition, (3) the Bose-Einstein condition.

Let us suppose the assembly to be distributed in equi-energy layers with the energy-interval $(\epsilon_s, \epsilon_s + d\epsilon_s)$ for each particle, and let N_s be the number of particles in this interval. The phase-volume occupied by each particle

$$g_s = 2\pi V (2m)^{3/2} \epsilon_s^{1/2} d\epsilon_s. \quad . \quad . \quad . \quad (2)$$

Then, according to Ehrenfest and Trkal,

$$G = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s}. \quad . \quad . \quad . \quad (3)$$

This theorem has been given by Ehrenfest and Trkal without proof, though to many it may not be so self-evident. We are therefore supplying a proof. Let G_N denote the phase-space described by N -particles, and G_{N-1} the phase-space described by $N-1$ -particles, the remaining particle being assigned to the region $(dx dy dz dp_x dp_y dp_z)$. We have

$$G_N = \frac{V^N (2\pi m)^{\frac{3N}{2}} E^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2} + 1\right)}. \quad . \quad . \quad . \quad (3')$$

Now we have ⁽⁸⁾

$$\frac{G_{N-1}}{G_N} = \frac{dw}{d\tau}, \quad . \quad . \quad . \quad (4)$$

where dw is the probability that the particle is to be found in the phase-volume considered. We have therefore

$$dw = \frac{N_s}{N},$$

and $d\tau$ the phase-volume of the particle under question $= g_s$. Thus

$$G_N = G_{N-1} \cdot \frac{g_s}{(N_s/N)}.$$

Then by successive application of the same theorem

$$G_N = G_{N-N_s} \left(N \frac{g_s}{N_s} \right)^{N_s},$$

and finally, taking all the energy-layers,

$$G_N = \prod_s g_s^{N_s} \left(\frac{N}{N_s} \right)^{N_s} \\ = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s} \quad \dots \dots \dots (3)$$

We have thus reduced the calculation of the phase-volume from the $6N$ dimensional space to one of 6 dimensions. We shall now show that the classical expression for entropy is easily obtained from this value of G . We have

$$W = \frac{1}{\prod_s N_s!} \prod_s \left(\frac{g_s}{h^3} \right)^{N_s}$$

Let $\frac{g_s}{h^3}$ be denoted by a_s ;

$$\begin{aligned} \text{then} \quad S &= K \log W \\ &= K \left\{ \sum_s N_s \log a_s - \sum_s N_s (\log N_s - 1) \right\} \\ &= K \sum_s N_s \log \frac{a_s}{N_s} + KN. \quad \dots \dots \dots (4) \end{aligned}$$

$$\begin{aligned} \text{Now} \quad E &= \sum_s N_s \epsilon_s \\ N &= \sum_s N_s \end{aligned} \quad \left. \vphantom{\begin{aligned} E &= \sum_s N_s \epsilon_s \\ N &= \sum_s N_s \end{aligned}} \right\} \dots \dots \dots (5)$$

Hence, applying the variation-principle,

$$\left. \begin{aligned} \delta S &= \sum_s \delta N_s (\log a_s - \log N_s) \\ \delta N &= \sum_s \delta N_s \\ \delta E &= \sum_s \delta N_s \epsilon_s \end{aligned} \right\} \dots \dots \dots (6)$$

$$\text{Therefore} \quad \log a - \log N + \lambda \epsilon_s + \mu = 0$$

$$\text{or} \quad N_s = \alpha a_s e^{\beta \epsilon_s} \quad \dots \dots \dots (7)$$

It can now be easily proved in the usual way that

$$\beta = -\frac{1}{kT}, \quad \text{and} \quad \frac{1}{\alpha} = \frac{V}{N h^3} (2\pi m kT)^{3/2}, \quad \dots \dots (8)$$

and substituting these values, we can easily show that S gets the classical value, viz.,

$$NK \log \left\{ \frac{V}{N h^3} (2\pi m kT)^{3/2} e^{5/2} \right\} \quad \dots \dots \dots (9)$$

Now we shall show how the Fermi-Dirac expression can be obtained from the definition of W .

The phase-volume of the assembly

$$G = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s}$$

has been calculated on the supposition that the phase-volume occupied by each individual particle is infinitely small compared with the total phase-volume at its disposal, viz., g_s . Let us now give up this assumption, and suppose it occupies a finite phase-volume " a ." Then

$$G = \frac{N!}{\prod_s N_s!} \prod_s g_s(g_s - a) \dots (g_s - \overline{N_s - 1}a). \quad (10)$$

The argument is just the same as that which we introduce in the calculation of the van der Waals's correction " b " from probability consideration. When each particle occupies negligible volume we have

$$W \propto V^N;$$

but when the volume " β " cannot be neglected,

$$W \propto \prod_{\gamma=1}^N (V - \overline{\gamma - 1}\beta).$$

In the above method we have introduced the phase-volume g_s instead of the space-volume V , and calculated G_N . Now

$$\begin{aligned} W &= \frac{G}{h^{3N} N!} \\ &= \frac{1}{\prod_s N_s!} \prod_s \left(\frac{g_s}{h^3} \right) \dots \left(\frac{g_s}{h^3} - \overline{N_s - 1}a \right) \\ &= \frac{1}{\prod_s N_s!} \prod_s a_s(a_s - \epsilon) \dots (a_s - \epsilon \cdot \overline{N_s - 1}), \end{aligned}$$

where

$$\epsilon = \frac{a}{h^3},$$

$$= \prod_s \frac{a_s!}{\overline{N_s!} (a_s - \epsilon N_s)!} \dots \quad (11)$$

If we put $\epsilon = 1$, we get the Fermi-Dirac expression for W ; when $\epsilon = -1$ we have

$$W = \prod_s \frac{a_s + \overline{N_s - 1}!}{(a_s - 1)! N_s!}, \quad (12)$$

which is the Bose-Einstein expression for W .

It may be mentioned here that the above discussion was originally inspired by an article of L. Brillouin (*Ann. d. Phys.* vii. 1927). But in spite of apparent resemblance, the method given here differs in essential points from Brillouin's. Firstly, Brillouin follows Bose-Einstein and Fermi-Dirac closely in calculating probability by making use of a_s (which is Brillouin's g_s) as the number of degrees of freedom which a particle can have when its energy lies between ϵ_s and $\epsilon_s + d\epsilon_s$. It may be easily shown that though we obtain the various values of N_s by subjecting Brillouin's expressions for W to the usual variational process in the three different cases (equations 21), they do not give us absolute values of entropy unless some assumption is made regarding the value of A or G in equation (21) of Brillouin. We have to make

$\frac{G}{a} = N$ in order to get the correct value of S . The justifi-

cation for this assumption is not clear, and Brillouin has made no attempt to calculate the absolute value of S . He devotes a good deal of discussion over the origin of the

permutability factors $\frac{N!}{\prod_s N_s!}$, which is quite unnecessary.

The factor comes out automatically when we calculate the total phase-volume of the ensemble not in $6N$ dimensions, but in 6 dimensions.

The above method has therefore the merit of giving a deduction for the absolute value of S on the three views from a unitary standpoint. The classical statistics and Fermi-statistics are easily understandable, and probably in the case of Fermi-Dirac statistics it affords a clearer physical view of the case than Fermi's original method. There may be many who share with us the difficulty in understanding the extension of the Pauli Principle, which has been shown to be the guiding principle in the formation of atoms out of protons and electrons, to the case of an ensemble of N independent particles possessing only translatory motion (*e. g.*, Hall, *Proc. Nat. Acad. Sci.* 1928). The deduction given here follows exactly the same lines as the deduction of the van der Waals's correction for finite volumes, and is therefore physically more comprehensible.

Of greater difficulty is the comprehension of the Bose-Einstein statistics. Here " a ," the phase-volume of any particle, has to be put negative ($-h^3$). These statistics have therefore to be definitely ruled out in the case of material particles. But as it is found to be correct in the statistics

of light-particles, we have to assume that when a photon enters a phase-space, the space expands, since the total phase-volume is increased by the phase-volume of the photon. A discussion will be found in Brillouin's paper above referred to.

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- (1) Bose, *Zeits. f. phys.* xxvii. p. 384 (1924). Einstein, *Sitz. Preuss. Akad.* p. 261 (1924); p. 3 (1925).
- (2) Fermi, *Zeits. f. phys.* xxxvi. p. 902 (1926). Dirac, *Proc. Roy. Soc. A*, cxii. p. 661 (1926).
- (3) Boltzmann, "Über die Eigenschaften Monozyklischer System." *Wien. Ber.* xc. (1884); *Wiss. Abhandl.* iii. Nr. 73, S. 132 ff.
- (4) Gibbs, 'Statistical Mechanics.'
- (5) Ehrenfest and Trkal, *Proc. Amst. Acad.* xxiii. (1920).
- (6) Planck, *Zeits. f. phys.* xxxv. p. 155 (1925).
- (7) Saha and Sur, *Phil. Mag.* i. p. 280 (1926).
- (8) Jeans, 'Dynamical Theory of Gases,' 2nd ed. chap. iv. pp. 58 62. Wassmuth, *Statistische Mechanik*.

LV. Application of the Photoelectric Cell to the Measurement of Small Displacements. By J. A. C. TEEGAN, M.Sc., Lecturer in Physics, and K. G. KRISHNAN, B.Sc., Demonstrator in Physics, University College, Rangoon*.

1. **A**N ingenious method of recording small displacement by means of a photoelectric cell is described by Cristescu †. The rays from a source of light rendered parallel by a collimator fall on two gratings mounted parallel, the one behind the other. The front grating is connected to the body the displacement of which is to be measured. When the spaces of the gratings coincide the light passes through and is focussed on the cell, the current being recorded on a sensitive galvanometer. A displacement of the front grating reduces the light, and the galvanometer deflexion is reduced. With gratings of only 5 lines per mm. a displacement of .1 mm. produces a deflexion of 10 galvanometer divisions.

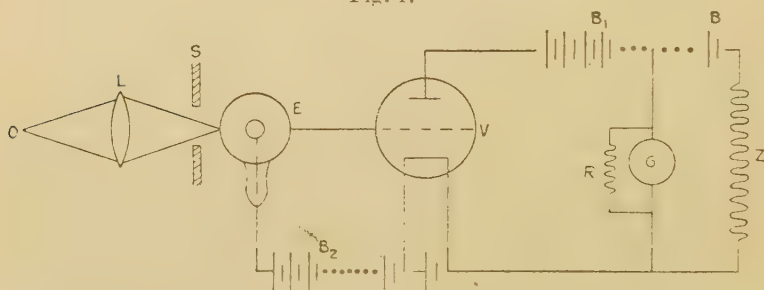
2. A method based on somewhat similar principles is described in this paper. Fig. 1 illustrates the general arrangement. Light from a "pointolite" source is focussed by the lens L on the photoelectric cell E

* Communicated by the Authors.

† Cristescu, *Phys. Zeits.* xxx. pp. 24-27 (1929).

(potassium vacuum type). A slit S is placed in the path of the beam just in front of the cell. The width of the slit is variable, and can be adjusted by means of a micrometer screw device reading to $\cdot 1$ mm. The quantity of light entering the cell is proportional to the area, and hence to the width of the slit. Assuming a linear relation between the photoelectric current and the illumination, the current is a linear function of the width of the slit if the slit when fully open (5 mm.) is uniformly illuminated (the attainment of this condition requires careful adjustment). The photoelectric current is amplified as shown, the valve being operated on the linear portion of its "characteristic." For small values of the photoelectric current the amplification is uniform, and the anode current is proportional to the width of the slit.

Fig. 1.

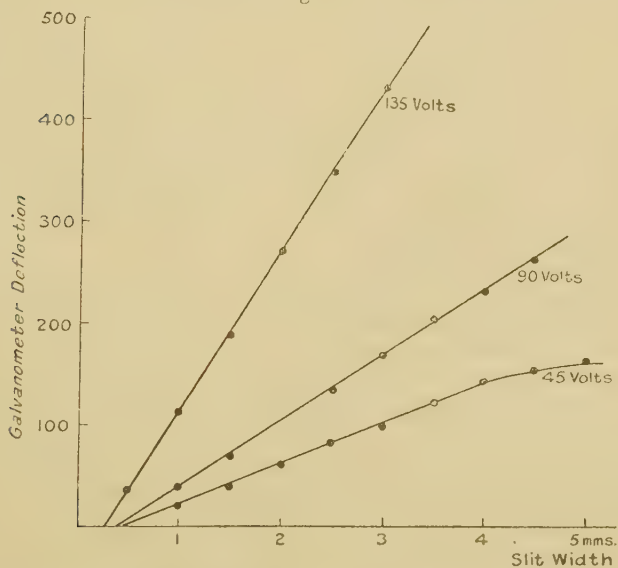


Initially, with slit closed the anode current is balanced by means of the potential compensating device ZB . If C is any value of the anode current a current $\frac{Z}{Z+G} (C-C_0)$ will flow through the galvanometer G , and for values of C close to C_0 a sensitive galvanometer can be used to measure C . This balancing device has the additional advantage of eliminating errors due to any "dark current" in the photoelectric cell.

3. In fig. 2 the variation of the anode current (galvanometer deflexion) with "slit width" is illustrated for different values of the photoelectric potential. In each case the deflexion is a linear function of the slit width, the sensitivity diminishing as the voltage on the cell is decreased. For a voltage of 135 volts a change in width of 1 mm. corresponds to a deflexion of 120 scale-divisions

(1 division = $\cdot 15$ microamp.). A movement of 1 mm. produces therefore an anode current variation of 17 microamps. On a unipivot Paul galvanometer this produces a deflexion of about 35 scale-divisions, and movements of $\cdot 1$ mm. can be determined with accuracy. Under these conditions extremely steady conditions have been obtained. On a sensitive mirror galvanometer (1 division = 10^{-9} amp.) a movement of 1 mm. would correspond to a galvanometer deflexion of 17,000 divisions.

Fig. 2.



4. In practice it has not been found possible to obtain such extremely high sensitivity, owing to unsteadiness. The unsteadiness is associated with

- (1) Fluctuation in high-tension and low-tension batteries.
- (2) External high frequency disturbances in the laboratory.
- (3) Fluctuation in the intensity of the light source.

The unsteadiness due to batteries can be reduced to a practical minimum by employing batteries of large capacity in perfect condition. A battery built up of small accumulator-cells is suitable for the high-tension source

of voltage ; it is also an advantage to tap off two or four volts from the anode battery B for use in the balancing circuit BZ. High frequency effects can be eliminated by careful screening, and the apparatus is being redesigned in a more compact form with a view to removing this source of disturbance. With a sensitive galvanometer shunted 10, we have obtained steady readings except for the slight and continual drift of the zero. One of the authors has investigated the possibility of eliminating this "zero drift" effect in a thermionic valve experiment of this type dealing with the measurement of air-stream velocities *. It arises from the falling off in the discharge rate of the batteries with time, and can be very successfully eliminated by using the current from a second thermionic valve to balance the main anode current instead of the battery B, both valves being supplied by the same H.T. and L.T. batteries. The incorporation of such a device in the present apparatus, however, considerably complicates the arrangement, and it is better to seek sensitivity by other means (see below).

5. The method of employing the present apparatus for recording small displacement is obvious. The movable portion of the slit is attached to the object the displacement of which is to be determined, the difference in the galvanometer deflexion before and after being a measure of the displacement. Except in experiments where the continual variation of a displacement is required, the "zero-drift" error is not of importance, as the zero can be redetermined each time an observation is made.

6. The possibility of increasing the sensitivity of the instrument is now being investigated, with a view to developing an ultra-micrometer on these principles. Very high and uniform amplification can be obtained by using a dull-emitter four-electrode valve † as an amplifier, and it is hoped in this way (using a more sensitive photoelectric cell) to increase the practical sensitivity to a great extent. The application of the method to that employed by Cristescu is also under investigation.

Physics Department,
University College,
Rangoon, Burma,
11th September 1929.

* Teegan, Phil. Mag., May 1926, pp. 1117-1121.

† D. T. Harris, Journ. Scientific Inst., Jan. 1929.

LVI. *Theory of Collision of Spheres of Soft Metals.*

By J. P. ANDREWS, M.Sc., F.Inst.P. (East London College)*.

ABSTRACT.

BEGINNING with the fact that when two spheres of soft metal collide, permanent deformation is produced when the velocity of approach exceeds a definite critical value ; and with the aid of the assumption that over the permanently deformed region the pressure remains constant at all points, a theory of collision is worked out. This theory is found capable of accounting for the variation with the velocity of approach v , of

- (a) The duration of contact t of the spheres,
- (b) the diameters d of the permanent deformations, and
- (c) the coefficient of restitution e .

The detailed character of the experimental results is explained.

At high speeds of approach, the duration of contact and the quantity e^2v^2 are linear functions of $\frac{1}{v}$ and of v respectively; while it appears that a definite quantity of energy is required per unit mass of the material apparently removed during deformation. A latent heat of deformation for a number of substances is calculated.

Finally, the influence of viscous resistance and of time-effects, such as the elastic after-effect etc., is considered.

IN a recent paper †, I have shown that when two exactly similar spheres are allowed to collide at different velocities v , the duration of their contact is calculable from an empirical formula of the type

$$t = t_0 + a/v^n,$$

where t is the duration of contact and t_0 , a , and n are constants. The diameters of the permanent deformations produced on the spheres when the velocity exceeds a value v_0 are represented by the following formula :

$$d = b(v - v_0)^m,$$

* Communicated by the Author.

† Phil. Mag. viii. p. 781 (1929).

b and m being constants characteristic of the material and the size of the spheres.

Further experiment upon imperfectly elastic spheres is available in the work of C. V. Raman* at low velocities of approach. By a photographic method the variation of the coefficient of restitution was investigated, and found to approach unity at very low speeds. The curves published by Raman are of the type shown in fig. 6.

A theory of collision, to be sufficient, must explain and correlate these results.

As a preliminary explanation and justification of the ideas involved in this theory, consider the hypothetical case of the impact of a pair of ideally plastic spheres; that is, spheres which remain permanently deformed whenever they come into contact. Whilst in contact these spheres will have a common plane of contact, touching each of the spheres in a circle of radius r (the circle of contact). The fundamental assumption of the present theory is that the pressure is the same, p_0 , at all points over this circular area of contact, and is independent of r .

The total force at any instant tending to separate the spheres is therefore $\pi r^2 p_0$. But if the distance between the centres of the spheres is $2R - 2S$, R being the radius of the spheres, $RS = r^2$, by Hertz's theory, so that the force is $\pi R p_0 S$.

The axis of S is the line joining the centres. Choose the origin as the point of intersection of the plane of contact with this axis; then, since the distance between the centres is $2R - 2S$, the coordinate of the centre of one of them is $R - S$, and we may write, if M is the mass of one sphere,

$$M \frac{d^2}{dt^2} (R - S) = \pi R p_0 S,$$

and if $n^2 = \frac{\pi R p_0}{M}$, the solution is $S = A \sin nt$, provided $S = 0$

when $t = 0$. Consequently $\frac{ds}{dt} = 0$, when $\cos nt = 0$, or

$nt = \frac{\pi}{2}$; that, is when

$$t = \frac{\pi}{2} \sqrt{\frac{M}{\pi R p_0}} \quad \dots \dots \dots (1)$$

Now allow the plastic spheres to be endowed with a very small elastic reaction, otherwise negligible, which will,

* C. V. Raman, Phys. Rev. xii. p. 442 (1918).

however, be just sufficient to separate the spheres after the relative velocity has been annulled. Then equation (1) gives the duration of the contact, and it will be observed that the velocity of approach does not affect its constant value.

The actual cases under consideration approximate to this state at very high speeds of approach; the duration of contact, therefore, should tend to a constant value as v becomes large. This agrees with experimental evidence.

From equation (1) we have the relation

$$p_0 t_0^2 = \frac{\pi M}{4R}.$$

Now p_1 , the least pressure required to initiate permanent deformation, may be calculated from Hertz's theory of perfectly elastic collision and the value v_0 of the velocity at which deformation was first produced. This may be compared with p_0 calculated from the last relation, using the value of t_0 derived from the experiments. The numbers are compared in Table I. (The calculation of p_1 differs from that in the former paper in that S_0 , the critical value of S , was calculated from the formula $5.984 S_0/v_0 = t_1$, where t_1 is the duration when $v = v_0.t_1$ was taken from the experimental curves.)

TABLE I.

| Substance. | p_0 (dynes/cm. ²). | p_1 (dynes/cm. ²). |
|-----------------|----------------------------------|----------------------------------|
| Aluminium | 2×10^9 | 3.4×10^9 |
| Tin | 1.2×10^9 | 2.1×10^9 |
| Babbitt | 2.6×10^9 | 1.1×10^9 |
| Lead-Tin | 4.8×10^9 | 1.1×10^9 |
| Brass | 2.2×10^{10} | about 5×10^9 |

Considering that

- (1) p_1 depends on v_0 , which can only be measured by extrapolation, sometimes rough;
- (2) the calculation of p_1 requires the knowledge of elastic constants whose values could not be obtained very accurately in some cases,

the agreement justifies us in identifying p_0 and p_1 . The idea of a constant pressure p_0 is supported by the work of J. H. Vincent*, in which steel balls produced indentations in lead plates.

* J. H. Vincent, Proc. Camb. Phil. Soc. 1898-1900.

DEVELOPMENT OF THE THEORY.

I. *Duration of Contact.*

We will assume that when v is less than v_0 , the velocity of approach at which permanent deformation commences, the spheres are perfectly elastic. The conditions are then exactly those visualized in Hertz's original theory, which may be taken over unchanged; and this leads to the following formula for the duration of contact:

$$t = 5.886 \left[\frac{5}{16} \frac{M}{k} \right]^{2/5} \cdot \frac{1}{v^{1/5}}, \quad \dots \quad (2)$$

where $k = \frac{\pi E}{3} \sqrt{R}$. E is an elastic modulus.

For velocities of approach exceeding the critical value v_0 , we may divide the process of collision into three periods:—

(a) *The elastic period.*

Until the stress at the centre of the circle of contact attains the value p_0 , all the retarding forces will be perfectly elastic. The time required to attain this stress will, however, depend on v , and we may call it t_a .

(b) *The plastic period.*

The spheres attain the stress p_0 while moving with a definite velocity which depends on v . Subsequently they are brought to zero relative velocity under the combined action of two forces: (1) due to the pressure p_0 evenly distributed over the central plastic area, and (2) an elastic force due to the strained annulus enclosed between the plastic circle and the circumference of the circle of contact. A time t_b will be required to reduce the spheres to zero relative velocity.

(c) *The return period.*

Instantly following the attainment of relative rest, the spheres begin to move apart. The accelerating forces are now everywhere elastic, since the stress within the plastic circle immediately falls to less than p_0 . The time required from zero relative velocity until the spheres finally separate is t_c .

The complete duration of contact is therefore

$$t = t_a + t_b + t_c.$$

The detailed calculation of these periods now follows, and we shall make continual use of two formulæ taken from Hertz's theory*, viz.:—

(a) The stress at any point within the circle of contact of radius r_0 at which the pressure p_0 is not yet attained is given by

$$\frac{E \sqrt{r_0^2 - r^2}}{2R},$$

where

$$E = \frac{4q}{\pi(1-\sigma^2)} \cdot \quad \begin{array}{l} (q = \text{Young's Modulus} \\ \sigma = \text{Poisson's Ratio}). \end{array}$$

(b) By integration, before any portion of the area in contact has attained the pressure p_0 , the total force tending to separate the spheres is

$$K = \frac{\pi E}{3R} (RS)^{3/2},$$

where $2R-2S$ is the distance between the centres of the spheres.

(a) *The calculation of t_a .*

Let the axis of S be the line joining the centres, and let the intersection of this with the plane of contact be the origin. If the distance between the centres after contact is $2R-2S$, the coordinate of the centre of one of them is $R-S$. The retarding force is, as quoted above,

$$K = kS^{3/2},$$

where

$$k = \frac{\sqrt{R}\pi E}{3}.$$

Hence, if M is the mass of one sphere,

$$M \frac{d^2}{dt^2} (R-S) = kS^{3/2}$$

or

$$\frac{d^2 S}{dt^2} + \frac{k}{M} S^{3/2} = 0.$$

Multiplying by $\frac{ds}{dt}$ and integrating,

$$\frac{1}{2} \left(\frac{ds}{dt} \right)^2 + \frac{2}{5} \frac{k}{M} S^{5/2} = \text{const.} \quad . \quad . \quad . \quad (3)$$

* *Vide* Love, 'Elasticity.'

Since, now, $\frac{ds}{dt} = v/2$ when $S = 0$, we have

$$\frac{ds}{dt} = \sqrt{\frac{v^2}{4} - \frac{4}{5} \frac{k}{M} S^{5/2}},$$

and the time t_a

$$= \int_0^{S_0} \frac{ds}{\left[\frac{v^2}{4} - \frac{4}{5} \frac{k}{M} S^{5/2} \right]^{1/2}},$$

where S_0 is the value of S at the moment p_0 is attained. Let ψ be the maximum value of S , which would have been reached had perfect elasticity reigned throughout. Then

$$\psi = \left[\frac{5}{16} \frac{M}{k} v^2 \right]^{1/5}.$$

t_a may then be reduced to

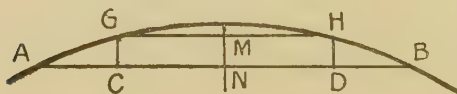
$$t_a = \frac{2\psi}{v} \int_0^{S_0/\psi} \frac{dx}{(1-x^{5/2})^{1/2}} \cdot \cdot \cdot \cdot (4)$$

Now $S < \psi$, so that the integral has to be computed for values of $\frac{S_0}{\psi}$ between 0 and 1. This was done numerically without difficulty.

(b) *The calculation of t_b .*

Let fig. 1 represent the portion of a sphere concerned in

Fig. 1.



a collision. Let $AB = 2r_0$ be a diameter of a circle of contact, and let $CD = 2r_1$ be a diameter of the plastic circle.

Stress at E, as before,

$$= \frac{E}{2R} \sqrt{r_0^2 - r^2}.$$

Force due to elastic annulus AC

$$= \int_{r_1}^{r_0} \frac{2\pi r E}{2R} \sqrt{r_0^2 - r^2} dr = \frac{E\pi}{3R} (r_0^2 - r_1^2)^{3/2}.$$

But as the pressure at C = p_0 , this force may be written

$$\frac{8}{3} \frac{\pi R^2 p_0^3}{E^2}.$$

It is noteworthy that this is constant, independent of the velocity of approach.

The force inside the annulus, due to the plastic circle, is $\pi r_1^2 p_0$, and as

$$r_1^2 = RS - p_0^2 \frac{4R^2}{E^2},$$

the total force is

$$\frac{8}{3} \frac{\pi R^2 p_0^3}{E^2} + R p_0 \pi S - p_0^3 \frac{4\pi R^2}{E^2} = R p_0 \pi S - \frac{4}{3} \frac{\pi R^2 p_0^3}{E^2}.$$

The equation of motion is consequently

$$M \frac{d^2 S}{dt^2} = - \left[R p_0 \pi S - \frac{4}{3} \frac{\pi R^2 p_0^3}{E^2} \right],$$

or, writing β for $S - \frac{4}{3} \frac{R p_0^2}{E^2}$,

$$\frac{d^2 \beta}{dt^2} + \frac{\pi R p_0}{M} \beta = 0.$$

And since (1) $S = S_0$ when $t = 0$,

$$(2) \frac{ds}{dt} = v_1 \quad \text{when } t = 0,$$

the solution is

$$\beta = A \sin (nt + \delta), \quad n^2 = \frac{\pi R p_0}{M}, \quad (5)$$

where

$$\tan \delta = \frac{1}{v_1} \frac{8}{3} \frac{R p_0^2}{E^2} \sqrt{\frac{\pi R p_0}{M}}$$

and

$$A^2 = \frac{M}{4\pi R p_0} v^2 + \frac{64}{9} \frac{R^2 p_0^4}{E^4} - \frac{4}{5} \frac{k}{\pi R p_0} S_0^{5/2}.$$

The velocity v_1 , at which the sphere enters on this stage, may be calculated from equation (3) thus :

$$v_1^2 = \frac{v^2}{4} - \frac{4}{5} \frac{k}{M} S_0^{5/2}.$$

From equation (5), $\frac{ds}{dt} = 0$ when $t = \frac{1}{n} \left(\frac{\pi}{2} - \delta \right)$.

So that

$$t_b = \sqrt{\frac{M}{\pi R p_0}} \left\{ \frac{\pi}{2} - \delta \right\}. \quad (6)$$

As a check, when v is very large, δ approaches zero, and t_b approaches the value

$$\frac{\pi}{2} \sqrt{\frac{M}{\pi R p_0}},$$

as in equation (1).

(c) *The calculation of t_c .*

We imagine that on release the part CD rises to GH (fig. 1) and stops there. This is an approximation of the same order as the others implicit in this theory. GH will then be the diameter of the permanent deformation. Let us suppose then that the diameter of the circle of contact at any instant is r_0 , and that $CN = GM = r_1$, the radius of the plastic circle.

The force due to the elastic annulus is, as before, $\frac{E\pi}{3R} (r_0^2 - r_1^2)^{3/2}$. If p is the stress at the edge of the plastic circle at any moment, p is also the pressure at all points within that circle, according to our previous notions. r_1 will remain constant.

The force due to the plastic circle, now non-plastic, is

$$\frac{\pi r_1^2 E}{2R} \sqrt{r_0^2 - r_1^2}.$$

Hence the total force

$$F = \frac{E\pi}{R} \left[\frac{(r_0^2 - r_1^2)^{3/2}}{3} + \frac{r_1^2}{2} (r_0^2 - r_1^2)^{1/2} \right].$$

If, then, we write $u = r_0^2 - r_1^2$, so that πu represents the area of the annulus, we may write the equation of motion

$$M \frac{d^2 u}{dt^2} = - E\pi \left[\frac{u^{3/2}}{3} + \frac{r_1^2}{2} u^{1/2} \right],$$

remembering that $r_0^2 = RS$.

Multiplying by $\frac{du}{dt}$ and integrating, we have, if $\frac{du}{dt} = 0$ when $u = u_0$,

$$\left(\frac{du}{dt}\right)^2 = \frac{2\pi E}{M} \left[\frac{2}{15} (u_0^{5/2} - u^{5/2}) + \frac{r_1^2}{3} (u_0^{3/2} - u^{3/2}) \right], \quad (7)$$

and

$$t = \int_{u_0}^u \frac{du}{\left(\frac{du}{dt}\right)}.$$

If we write $\frac{u}{u_0} = x$, this is reducible to

$$t_c = \sqrt{\frac{M}{2\pi E}} \cdot u_0^{1/4} \int_0^1 \frac{dx}{\sqrt{\frac{2}{15} u_0 (1 - x^{5/2}) + \frac{r_1^2}{2} (1 - x^{3/2})}}. \quad (8)$$

This integral has to be calculated graphically for each value of r_1^2 ; that is, for each value of the velocity of approach, since r_1 is a function of v .

From the fact that the pressure at G is p_0 at the instant of greatest compression, we derive that

$$u_0 = r_0^2 - r_1^2 = \frac{4p_0^2 R^2}{E^2},$$

a constant quantity, independent of the velocity of approach. From this result and the maximum value of S , derived from equation (5), it is easy to show that

$$r_1^2 = R \sqrt{\frac{M}{4\pi R p_0} v^2 + \gamma} - \frac{8}{3} \frac{R^2 p_0^2}{E^2}, \quad \text{. . .} \quad (9)$$

where

$$\gamma = \frac{64}{9} \frac{R^2 p_0^4}{E^4} - \frac{4}{5} \frac{k S_0^{5/2}}{\pi R p_0}.$$

The complete duration of contact is now calculable from the three equations (4), (6), and (8).

II. The Diameters of the Permanent Deformations.

r_1 is the radius of deformation. Consequently equation (9) gives the variation of this quantity with velocity of approach.

III. The Coefficient of Restitution e .

The velocity of separation $\frac{1}{R} \frac{du}{dt} = \left(\frac{ds}{dt}\right)$ may be obtained from equation (7) by putting $u = 0$; for at that instant when $r_0 = r_1$, we are imagining the spheres to separate.

$$\left(\frac{du}{dt}\right)^2 = \frac{2\pi E}{M} \left[\frac{2}{15} u_0^{5/2} + \frac{r_1^2}{3} u_0^2 \right], \quad . \quad . \quad (10)$$

the value of r_1^2 coming from (9).

The ratio of the velocity of separation to the velocity of approach gives e .

NUMERICAL ILLUSTRATION.

In order to bring out the salient features of the theory, all the required quantities were computed for a typical case invented for the purpose, for which the following are the data :—

$$\begin{aligned} p_0 &= 5.5 \times 10^9 \text{ dynes/cm.}^2, \\ \text{Young's Mod. } \dots q &= 5.85 \times 10^{11} \text{ dynes/cm.}^2, \\ \text{Poisson's Ratio } \dots \sigma &= 0.3, \\ R &= 4 \text{ cm.}, \\ M &= 660 \text{ gm.} \end{aligned}$$

This is an example approximating to the actual case of Aluminium in my experiments. An attempt at exact comparison is, however, out of the question, because v_0 , which plays such an important part in the theory, could only be determined approximately, and a small variation in its value has an important influence in the calculations. From these values we derive

$$\begin{aligned} E &= 8.20 \times 10^{11} \text{ dynes/cm.}^2, \\ k &= 1.72 \times 10^{12}. \end{aligned}$$

The critical velocity v_0 , at which permanent deformation commences

$$\begin{aligned} v_0 &= 10.75 \text{ cm./sec.}, \\ u_0 &= 2.88 \times 10^{-3} \text{ cm.}^2, \\ \gamma &= -4.4 \times 10^{-8}. \end{aligned}$$

From these all the other useful quantities may be obtained.

The computations required for the integrals were performed graphically and may be left undescribed. Their results are summarized below.

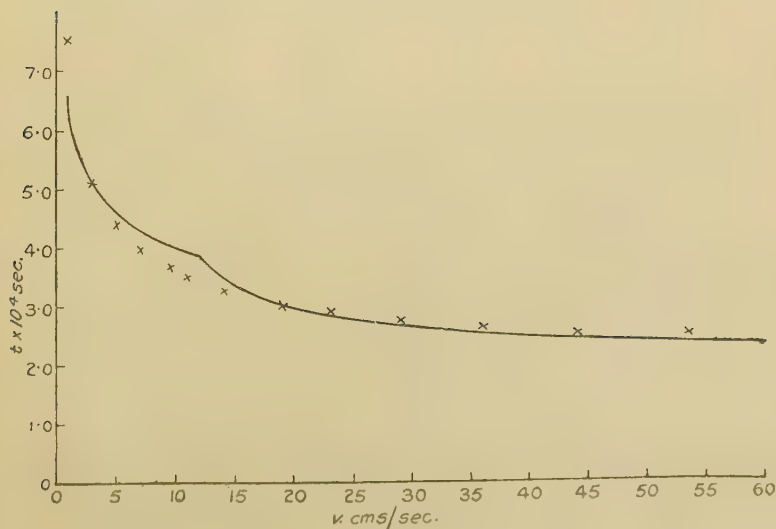
I. The Duration of Contact.

TABLE II.

| v cm./sec. | t_a $\times 10^4$. | t_b $\times 10^4$. | t_c $\times 10^4$. | Total sec. $\times 10^4$. |
|-----------------|--------------------------|--------------------------|--------------------------|-------------------------------|
| 1.0 | — | — | — | 6.34 |
| 2.0 | — | — | — | 5.52 |
| 4.0 | — | — | — | 4.81 |
| 6.0 | — | — | — | 4.43 |
| 8.0 | — | — | — | 4.18 |
| 10.0 | — | — | — | 4.00 |
| 12.0 | 1.48 | 0.49 | 1.78 | 3.75 |
| 15.0 | 1.06 | 0.80 | 1.47 | 3.33 |
| 19.0 | 0.805 | 0.99 | 1.21 | 3.005 |
| 24.0 | 0.62 | 1.12 | 1.07 | 2.81 |
| 30.0 | 0.48 | 1.21 | 0.96 | 2.65 |
| 37.0 | 0.40 | 1.27 | 0.84 | 2.51 |
| 45.0 | 0.325 | 1.32 | 0.76 | 2.405 |
| 60.0 | 0.25 | 1.37 | 0.65 | 2.27 |

These results are represented by the full curve of fig. 2.

Fig. 2.



The outstanding features of the curve are :

- (1) Its evident tendency to a constant value $t = t_0$;
- (2) the pronounced alteration in direction at $v = v_0$.

This last appeared at first sight to be a new prediction ; but I find that my experimental results practically all show such a tendency. In the account of these experiments no explanation was forthcoming, and I had assumed that experimental error must have entered to a greater extent than I could account for, since attempts to "improve" the curve by more careful observation did not succeed. In fig. 3

Fig. 3.

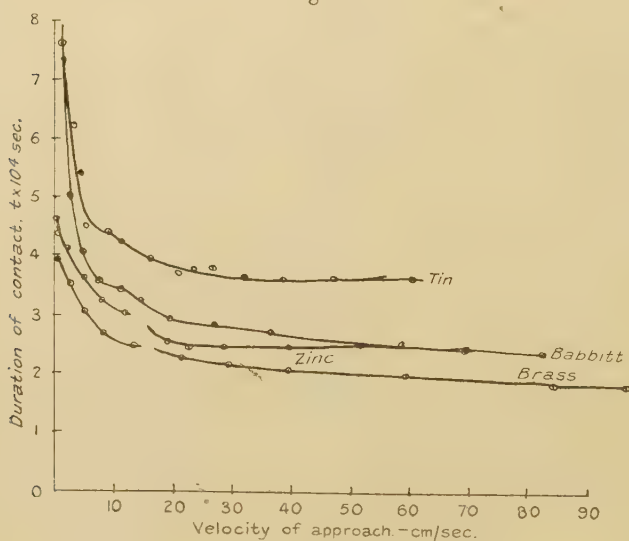


TABLE III.

| Substance. | $(v_0)_1$ cm./sec. | $(v_0)_2$ cm./sec. |
|-----------------|-----------------------|-----------------------|
| Aluminium | About 12 | About 8 |
| Tin (2) | 2.5 | 5 to 7 |
| „ (3) | 3 to 7 | 8 |
| Babbitt | 10.0 | 10.0 |
| Zinc | 9 to 10 | 12 |
| Lead-Tin | 0 to 4 | Cannot be detected. |
| Brass | 8.0 | (c.) 15 |

are re-drawn some experimental curves exhibiting the effect to a greater or less degree. Table III. shows the values of

v_0 derivable from the two methods, $(v_0)_1$ being obtained from the measured diameters of the deformations, and $(v_0)_2$ from the effect just described. The table will also serve to indicate to what extent the value of v_0 so obtained may be relied on.

An explanation of the constants in the empirical equation $t = t_0 + a/v^n$ may now be sought. t_0 appears quite clearly to be the value $\frac{\pi}{2} \sqrt{\frac{M}{\pi R p_0}}$ of equation (1).

To interpret the remaining part, the curve of fig. 2 was subjected to the same process as the experimental curves of fig. 3, namely an empirical equation of the required type was fitted to it, employing $t_0 = \frac{\pi}{2} \sqrt{\frac{M}{\pi R p_0}} = 1.535 \times 10^{-4}$. This gave, as a reasonably fair fit,

$$t = 1.535 \times 10^{-4} + \frac{6.03 \times 10^{-4}}{v^{0.47}},$$

the curve for this equation smoothing over the characteristic bend at v_0 . The crosses in fig. 2 are calculated from this equation. The agreement is similar to that given by similar equations with the experimental results. It is clear, then, that a and n have no special significance, and their values cannot yield any useful information after the manner of t_0 . The fact that the first part of the curve represents perfectly elastic collision is obscured by this formula.

II. The Diameters of the Permanent Deformations.

In fig. 4 are plotted the calculated values of the diameters d and the velocities of approach. The crosses are values from an empirical formula derived from these calculated results, $d = 2.938 \times 10^{-2}(v - v_0)^{0.487}$. It will be remarked how closely the theory accounts for the empirical equation. In the example worked out it is possible to say definitely that the index 0.487 is not 0.500, although so close. Reference to my previous paper will show that this agrees completely with experiment.

III. The Coefficient of Restitution.

Fig. 5 shows the variation of the coefficient of restitution as the velocity of approach varies. Fig. 6 gives for comparison some curves from C. V. Raman's results. The

general similarity is evident, and the portion on the experimental curves indicating a coefficient of restitution equal to unity is reproduced by the theory.

Fig. 4.

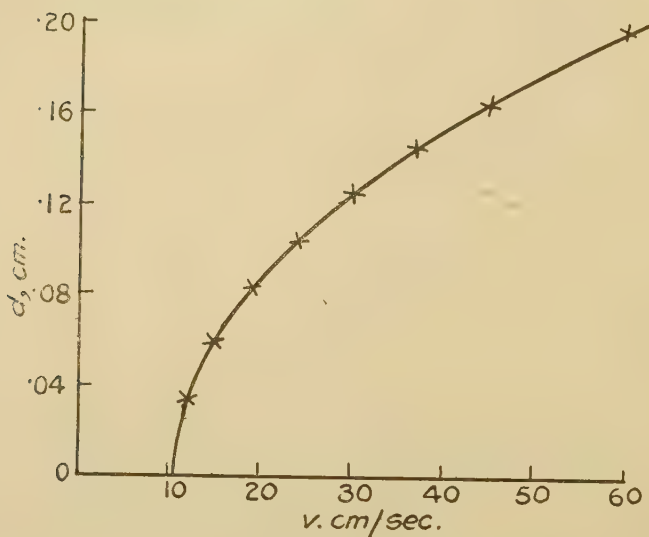
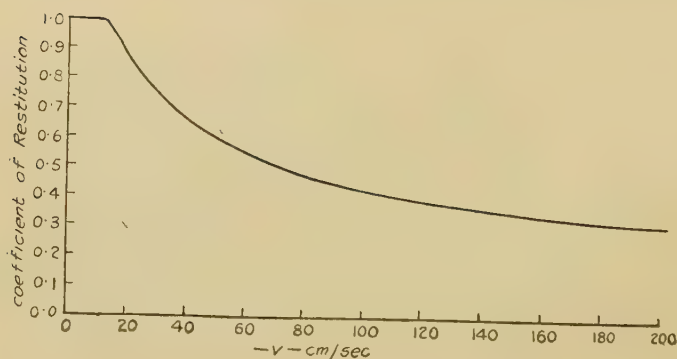


Fig. 5.



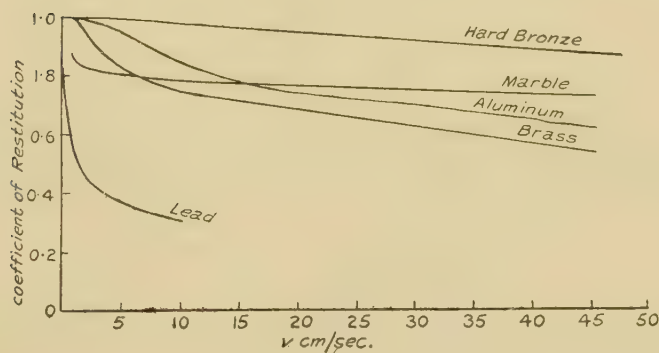
DISCUSSION OF THE THEORY.

The success with which the theory accounts for a number of different experimental results tends to justify the otherwise rather arbitrary assumption of perfect elasticity when the

velocity of approach is less than v_0 . It is a fact that the first few of my observations, that is, at low velocities, are the least accurate, and special experiments are in progress to test the hypothesis at such speeds. Nevertheless, in most cases the inverse fifth-power law for the duration of contact is approximated to.

When v is large compared with v_0 a number of simplifying approximations are possible, which lead to several instructive deductions. These approximate results are, for the sake of

Fig. 6.



brevity, merely summarized below. The values to which t_a , t_b , and t_c , respectively, approach at high speeds are

$$t_a = \frac{8R}{\lambda^2} \cdot \frac{1}{v},$$

$$t_b = t_0 - \frac{16R}{3\lambda^2} \cdot \frac{1}{v},$$

$$t_c = 0;$$

the complete duration of contact is therefore approximately

$$t = t_0 + \frac{8R}{3\lambda^2} \cdot \frac{1}{v},$$

and we have the approximate relation $(t - t_0)v = 8R/3\lambda^2$, where $\lambda = E/p_0$.

For the approximate diameters of the permanent deformations at high speeds we have

$$d_1^2 = 4Rt_0v/\pi - 32R^2/3\lambda^2,$$

or, at even higher speeds,

$$d_1^2 = \frac{4R}{\pi} t_0 v.$$

From this it follows that the volume of the spherical cap apparently removed when the sphere is deformed is proportional to the kinetic energy of the approaching sphere at very high speeds. This is like the rule first laid down by J. H. Vincent for the case of steel balls dropped into lead plates.

We have

$$(\text{vol. of cap}) = \frac{1}{8\rho_0} \cdot (\tfrac{1}{2} Mv^2),$$

or, mass apparently removed, $\frac{\rho}{8\rho_0} (\tfrac{1}{2} Mv^2)$, where ρ = density.

In other words, the energy per gram measured in heat units required to remove the material—what might indeed be called the latent heat of deformation of the material, L —is

$$\frac{8\rho_0}{\rho \times 4.2 \times 10^7} \text{ cal. per gm.}$$

In Table IV. are tabulated the values of this quantity for the substances used in my experiments. These are to be considered as only approximate values.

TABLE IV.

| Substance. | Al. | Sn. | Zn. | Babbitt. | Lead-Tin. | Brass. |
|-----------------|-----|-----|-----|----------|-----------|-----------|
| L cal./gm. | 70 | 16 | 120 | 34 | 52 | About 200 |

It should be emphasized that the elastic constants do not enter into this matter, which evidently is a phenomenon characteristic of the plastic condition.

When $v^2/3$ is not much larger than p_0^5/E^4R , the square of the velocity of separation has the value

$$w^2 = -\frac{512}{45} \frac{\pi R^3 E}{M \lambda^5} + \frac{32 \pi E R^2}{3 M \lambda^5} \sqrt{\frac{M}{4 \pi R p_0}} \cdot v \left(1 - \frac{64 \pi R^2 p_0}{15 \lambda^4 M v^2} \right);$$

but when $v^2/3$ is much larger, the last term in brackets approximates to unity, and we are left with the rule that $e^2 v^2$ is a linear function of v :

$$e^2 v^2 = av - b.$$

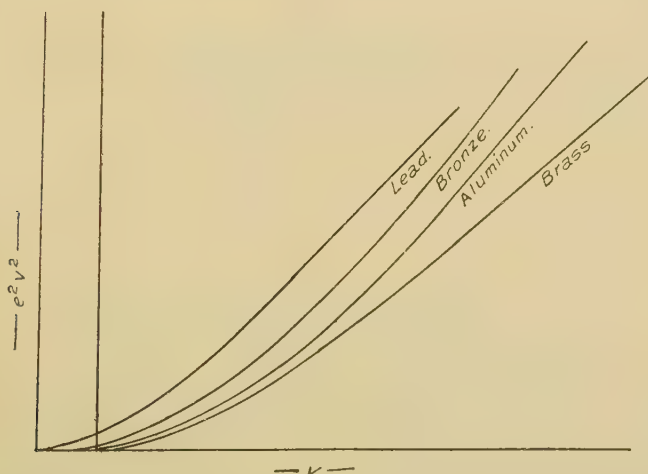
Moreover, at such speeds $a^2/b = 5.02$ for all spheres.

In fig. 7 are plotted Raman's experimental results, using e^2v^2 as ordinate and v as abscissa. The tendency to linearity at high speeds is noteworthy as confirming the theory. The ratios a^2/b are, however, in no case 5.02, but always smaller. This we should anticipate if $v^2/3$ is not much greater than p_0^5/E^4R . It is impossible finally to decide this point, since no data are available regarding the spheres used in Raman's experiments.

CONCLUDING OBSERVATIONS.

The assumption, fundamental to this theory, that the pressure is constant over the plastic circle is equivalent to

Fig. 7.



saying that the material of which that circle is composed, acts like a liquid. It must, moreover, behave like a very mobile liquid, for any differences of pressure have to be equalized in about 10^{-4} sec. under a pressure of a thousand atmospheres. It is almost inconceivable at first sight that the large viscous forces which must enter do not appear to have any marked final influence. That plastic material is actually moved seems more likely, in so far as a pronounced rim always surrounds the plastic circle as though material had been exuded. The key to the difficulty of this motion, and probably to that of the viscous resistances produced, appears to be the very small quantity of matter to be transported and the large pressure gradients available.

A gradient as large as 10^8 dynes per cm.² per cm. from the centre of the plastic circle outwards would only mean a variation of about 1 per cent. in the value of the normal pressure p_0 across this circle. The viscous effect would only tend to increase such a gradient, which, it appears, is never raised sufficiently high to interfere seriously with the constancy of the normal pressure p_0 .

Finally, it is worth remarking that collision experiments are among the few in the domain of elasticity into which time-effects, such as the elastic after-effect, fatigue, etc., do not enter to any appreciable extent. It is no doubt partly due to this fact that a simple explanation such as that given in this theory is possible, while the interpretation of experiment, so complex in other elastic problems, becomes in this case much easier.

During the development of this theory I have had the benefit of Prof. Lees's criticism, and have pleasure in recording my thanks.

LVII. *Some Phenomena of the Contact of Solids.*

By WILLIAM STONE *.

THE publication of a paper† by G. A. Tomlinson on "Molecular Cohesion" has recalled to my memory some experiments on this subject which I made in 1922, and an account of which I gave in a lecture (unpublished) before the Royal Society of Victoria, Australia, in August, 1923. The experiments were similar to Mr. Tomlinson's but had a considerably wider scope and, in certain respects, led to conclusions different from his.

The object of the experiments was to secure preliminary data for an experimental study of "solid friction." It was hoped that light might be thrown on the questions of when and under what conditions contact of solids takes place, and of the nature and magnitude of the forces acting between bodies in, or nearly in, contact—forces over which the experimenter has no control.

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

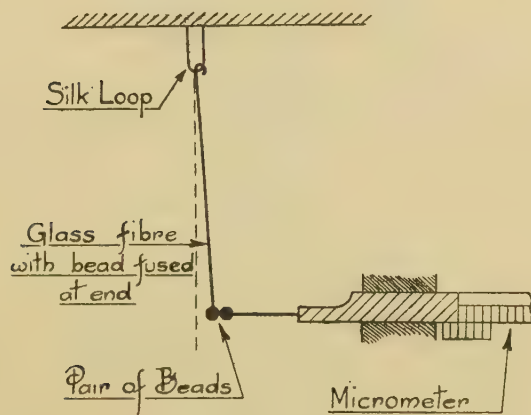
† Phil. Mag. vi. p. 695 (1928).

The principle of the method of experiment is illustrated in fig. 1.

By moving the bead attached to the micrometer, the suspended bead could be deflected, if there were adhesion between the beads, and the amount of deflexion measured. Consequently, the force tending to separate the beads could be directly estimated. For certain experiments, the bead apparatus was mounted in a chamber at the top of a specially designed electroscope as illustrated in fig. 2 and described later.

In the main series of experiments, the bodies tested for adhesion were small glass beads, one or two millimetres

Fig. 1.



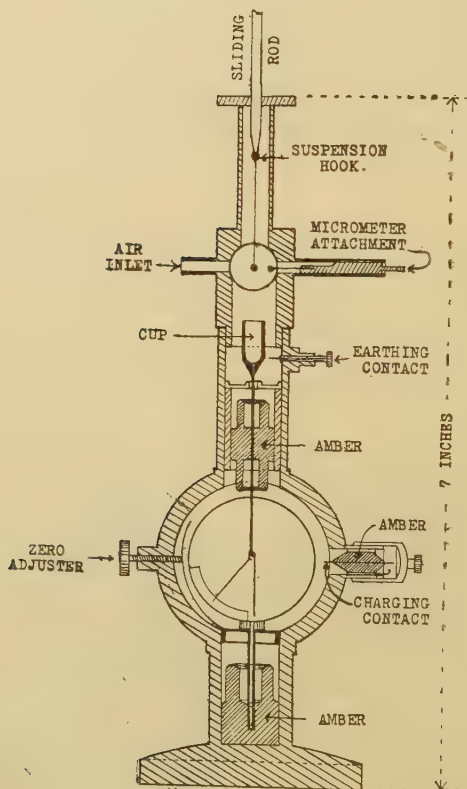
Principle of Experimental Method.

in diameter. The beads were specially made by the following process.

Glass rod was thoroughly washed, and drawn out after heating over a good Bunsen flame. The fibre so drawn out was cut, and the two ends so formed were fused into beads to constitute one pair. The beads were formed in a small blue gas flame, the oxidizing part being used. The burner consisted of glass tube drawn into a capillary and mounted horizontally, so that the glass fibre could be held approximately vertical and in the flame from the horizontal gas jet.

The fibre remote from the beads was held in steel tweezers, the points of which had just been made red hot. The fibre was then cut the desired length, and a small hook was formed on its free end if this was required to suspend the bead.

Fig. 2.



Section through axis of Electroscope.

The beads made in this way were assumed to be clean. As soon as each bead was made, it was placed in the apparatus in which it was to be tested.

Many different kinds of glass were used. Speaking generally, one type of glass gave the same results as another but there were one or two remarkable exceptions (page 619).

Adhesion in a Natural Atmosphere.

The earlier experiments were made in the natural atmosphere of the room. In this case, beads of each of the kinds of glass employed adhered when newly made; but lead glass beads only adhered feebly and, in a few cases, not at all.

Beads which had been contaminated by handling, or by being left exposed on the table, usually would not adhere when brought into contact. If, however, these beads were breathed on while they were in contact, strong adhesion at once took place, of the same order of magnitude and as lasting as that obtained with beads newly formed. If the beads were then forcibly separated, they would seldom adhere again until they had once more been breathed upon, or cleaned by heating or otherwise. Contaminated beads, after being made red hot, behaved like those freshly made. Clean beads, also, adhered after being breathed on in contact. Separation did not take place even though a force of from 5 to 10 per cent. of their weight tended to cause them to do so.

Any of the beads, whether (*a*) clean or (*b*) contaminated and breathed on, could be made to slide one over the surface of the other although acted on by a force tending to separate them. In most cases, as soon as the motion started the beads slid over each other in a manner which suggested that their surfaces were lubricated and that they were held together as by a force of mutual attraction. The force tending to separate them was about two-thirds of that which a first test showed would separate them.

Adhering beads which have been newly formed, and contaminated beads which have been breathed on when in contact, will continue to adhere for several days if they are protected from draughts of air by a suitable glass shade, even though the force tending to separate them is from 50 per cent. to 75 per cent. of that which will separate them.

In fine, freshly made beads (whether breathed on or not, while in contact) or contaminated beads that have been breathed on while in contact adhere, and forces of at least 10 per cent. of their weight are required to separate them.

They will sustain forces of one half to three-quarters

of this amount for indefinitely long periods—several days, at all events.

In looking for possible explanations of the phenomena observed, the following points were kept in view :—

- (a) true adhesion of uncontaminated glass with glass ;
- (b) surface tension of a film of water or other liquid between the beads ;
- (c) general electrification of the beads, or local electrification at or near the area of contact ;
- (d) adhesion due to contaminating matter not removable from the glass by recognized methods of cleaning.
- (e) gravitational forces.

A simple calculation will show that the forces found to exist far exceed the gravitational force of attraction, so that this force can only play a negligible part.

With respect to *surface tension*, an attempt was made to drive off any adsorbed liquid film between the beads by the application of heat from a gas flame. It was expected that this would also remove electrification except from the area of contact and possibly that immediately adjacent to it.

In one set of tests, newly formed soft German soda glass beads were mounted and brought into contact. The areas of contact were then subjected to tension as usual by moving the micrometer. A very small gas flame (the gas issuing from a capillary gas jet), from 2 to 3 mm. high, was then placed about 3 cm. from the glass beads and vertically below them and was kept there until it was judged that the beads had attained a steady temperature. No visible effect was produced.

The gas jet and flame were then raised in short steps at intervals of about 15 seconds, without any visible effect, until finally the faint colour of sodium flame appeared above the beads. The flame was kept in this position until the beads attained a dull red heat, whereupon instead of separating they drew together and ultimately fused into a solid mass (fig. 3).

Exactly similar effects were obtained with beads which had been contaminated and breathed upon.

Many pairs of beads (from soft German soda glass) were tested in this manner : always with the same results.

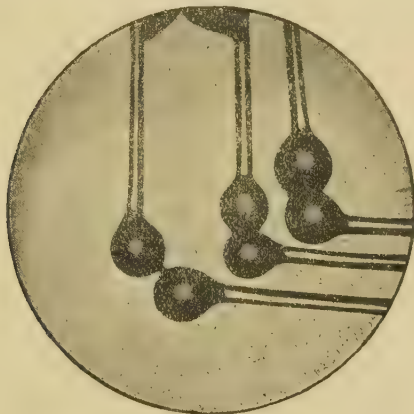
It had been anticipated that gases or vapours would be evolved at the surfaces of contact of the beads which had been breathed on and that the beads would then separate. This expectation was in no case realized.

Beads of certain kinds of glass did not fuse in the way just described until they had been breathed on and then heated more quickly.

Beads of other kinds of glass, again, did not draw together. Fine necks formed between them, which drew out and finally fused.

It must be borne in mind that, at the comparatively high temperatures of fusion, we are no longer dealing with solid bodies, but with highly viscous fluids.

Fig. 3.



As regards *electrification*, attempts were made to remove possible electrical charges from the beads by passing a Bunsen flame over them and over the glass fibres still attached to them, before bringing them into contact. The beads were then brought into contact and the flame was again passed over them. After this treatment, the phenomena were the same as those already described.

The beads and fibres were then breathed on whilst separated, and the fibres were earthed. Again no change of behaviour was observed. A gold leaf electroscope was instantly discharged when a similar piece of glass fibre, 10 to 15 cm. long, was breathed on and quickly brought into contact with the plate of the instrument.

When dried with a gentle heat, these fibres would only cause a very slow fall of the gold leaf.

Adhesion in an Atmosphere Artificially Dried.

It seemed desirable that more elaborate experiments should be made with a view to throwing light on

- (i.) the part possibly played by water in some form ;
- (ii.) the electrical state of the beads.

As regards (i.), the researches of Langmuir and others have clearly demonstrated the very great, indeed the almost insuperable difficulty of removing all water molecules from the surface of glass. It seemed therefore desirable that all possible precautions should be taken to ensure that the bead surfaces were as dry as they could be made.

At the same time, it was important to have facilities for testing the electrical state of the beads while the experiments were going on.

Both of these objects were secured with the help of the specially constructed piece of apparatus shown in fig. 2, comprising a chamber through which dry air could be passed and an electroscope by which a bead suspended in the chamber could be tested for electrification at any moment.

The suspended bead could be raised or lowered between limit stops by means of a balanced arm not attached to the electroscope. The horizontally mounted bead could be moved by means of a micrometer supported on an independent pillar. The air inlet, earthing plunger, sliding charging contact, and zero adjustment, are shown in the figure. The gold leaf was about 1.5 cm. long and not quite 1 mm. in width.

The deflexions of the gold leaf and distances between the two beads were measured by means of microscopes independently mounted.

The observation chamber had two opposite circular windows glazed with selected microscope cover-glass.

When the suspended bead was being tested for electrification the horizontal bead was drawn back by means of the micrometer screw and the suspended bead was lowered almost to the bottom of the cup attached to the conductor from which the gold leaf is suspended.

To charge the electroscope, the cap covering the "charging contact" was removed, and the contact wire pressed into contact with the inner chamber. The "earthing contact" was also pressed in. The charge was given from a rubbed rod of glass or ebonite until the desired initial deflexion of the gold leaf was produced. The "charging contact" was then drawn back by means of the small hook on it, the cap put on to protect the instrument from induction disturbances, and the "earthing contact" withdrawn.

The insulation by amber was fairly good. The fall of the gold leaf due to leakage was tested after the experiments herein referred to were terminated. At the end of three months the deflexion of the gold leaf was about 50 per cent. of its value at the commencement of the test.

A great many experiments were made with glass beads in the observation chamber above this electroscope. The effects looked for were:—

- (i) attraction at a distance ;
- (ii) adhesion ;
- (iii) electrification of the suspended bead.

In all cases the chamber enclosing the gold leaf was positively charged.

The radius of swing of the suspended bead was about 2.2 cm.

The capacity of the electroscope was about 4 cm.

The electroscope was roughly calibrated by using a brass sphere of 0.177 cm. radius suspended by a cocoon silk fibre. It was charged by bringing it into contact with the end of a fine wire connected to the + terminal of a few dry cells. The terminal P.D. of the battery was determined with an ordinary commercial voltmeter. The brass sphere was then put in the place of the suspended glass bead and lowered into the electroscope. Care was taken to keep other conductors at a considerable distance from the brass sphere when charging it.

The observations, in particular the deflexions of the gold leaf and the distance between the nearest points of the two beads after separation, were recorded in scale-divisions of the eyepiece micrometers used, and could of course be reduced to absolute measure. It is unnecessary to give the actual figures here.

The current of air through the chamber could be increased or decreased at will. The air on its way to the chamber was bubbled through sulphuric acid, mainly to enable its rate of flow to be checked, and then through two glass tubes, the first completely filled with freshly prepared calcium chloride for a length of 75 cm.; the second completely filled with phosphorus pentoxide for a length of 9 cm.

When taking the attraction at a distance, a scale-division line was made just to touch the suspended bead. This bead was then watched carefully and the horizontal bead was advanced to it. A movement of the suspended bead of 0.2 of a scale-division could easily be detected, corresponding to a movement of 0.003 mm., or a force of about 0.00014 of the weight of the bead. The largest suspended bead referred to in this paper was 1.72 mm. in diameter; taking the density of glass as 2.5, the weight of the bead is 0.00666 gram, and the horizontal component of the force 0.00000093 gram for a deflexion of 0.2 of a scale-division.

The general procedure with this apparatus was first, before the dry air was turned on, to bring the bead attached to the micrometer into contact with the suspended bead. Adhesion then regularly took place. Next, the dry air was turned on. When the beads had been exposed to the action of the dry air for some time, the micrometer bead could be brought up to the suspended one and drawn away again without any sign of adhesion. This condition of no adhesion could be steadily maintained so long as the current of dry air was kept going. When the dry air was turned off again, the beads at once began to show adhesion when brought together and the distance to which the suspended bead could be drawn over without losing contact with the other increased rapidly. It reached its normal value in a few minutes.

At times, a pair of adhering beads were drawn over by the micrometer so as to produce a force tending to separate them. The dry air was then turned on. The dry air caused the silk suspending loop to contract and draw the suspended bead over the surface of the other. These movements took place for some time in steps, but usually did not cause the beads to separate.

While watching the behaviour of the beads in the observation chamber, one had the distinct impression that

adhesion only occurred when there was something on the beads—say an electric charge or a water film—which could be removed or at least changed by the action of dry air.

Subsidiary experiments on the conductivity of water films, adsorbed on rods made from the same samples of glass as the beads, showed clearly that the free water on their surfaces is quickly removed by the action of dry air around them. On the other hand, no evidence of the electrification of soft German soda glass beads was detected at any time during the conduct of the experiments.

The absence of attraction at a distance, of adhesion in very dry air, and of any deflexion of the gold leaf of the electroscope, all strongly suggest that water, in some form, exercises an important influence on the adhesive properties of glass with glass.

It may be noted, however, that beads made from Jena combustion tubing showed phenomena differing widely from those observed with beads of the other samples of glass experimented with. These beads, when first put into the observation chamber, showed strong adhesion, and, after the first separation, strong electrification. When the beads were then exposed to the air of the room and the test repeated, they were found to be completely discharged, but they soon acquired a small charge of the opposite sign from before. After turning on dry air, the electrification of the suspended bead again changed sign, and it continued to increase with each contact between the beads.

No Adhesion Between Beads Immersed in Water.

A few experiments were made with glass beads immersed in water.

The beads were mounted in a vertical tube with a flat glass window. The tube and contents were mounted on a tilting table such as is used for testing level tubes.

By altering the tilt, the suspended bead was made to press against the other bead and was left in this position for some time. The tilting table was then brought very slowly to its zero position, and then a little further—far enough, if the bead were free, to cause a separation of a few hundredths of a millimetre.

In every case the beads separated, but in some cases intervals up to half an hour elapsed before light could be seen between the beads with the aid of a microscope.

Absence of Mechanical Injury to Surfaces.

Many beads were subjected to careful microscopical examination with a view to ascertaining whether they had received mechanical injury such as has been described by Hardy and others.

So long as the only force pressing them together was their mutual adhesion, not one case of injury to the surfaces which had been in contact was detected.

Many of these beads, after their first examination, were again caused to slide over each other, this time with some added force applied by hand. In these cases, tearing of the surfaces usually took place and the appearance of the damage, as seen by the microscope, was in all respects similar to that described by Hardy and recently by Tomlinson.

Summary.

The conclusions to which these experiments seem to point are these :—

(1) In the case of glass, adhesion is due to the presence of water molecules entangled in the surface layer of the glass. That the adhesion is due to water molecules seems proved by the fact that, in air which was artificially maintained in as dry a condition as possible, the adhesion phenomena practically disappeared.

(2) If water molecules once become entangled in the surface, they are difficult to remove. They can be removed by a current of dry air, so long as the beads are separate, but if the water molecules are entangled in the region of contact between two glass beads that are touching, it is extremely difficult to get rid of them by any of the ordinary means of drying, so that adhesion shows itself and persists—even though the beads be heated until they fuse together.

(3) The phenomenon of adhesion may or may not be accompanied by electrical effects. In the case of German soft soda glass it is not ; in the case of Jena combustion glass, it is.

(4) There is no adhesion between beads immersed entirely in water.

(5) Surfaces of contact are *not* injured so long as the only forces acting are those of natural adhesion.

LVIII. *On the Probability Method in the New Statistics.*

By S. CHANDRASEKHAR *.

(1) *Introduction.*

PROBLEMS in statistical mechanics can in general be treated by two methods. One is the method of the kinetics of collisions and the establishment of a H-theorem ; the other is the method of counting the complexions. Both these methods have been incorporated into the quantum statistics †.

Recently, however, a new method has been developed—"a geometrical weight method"—by W. S. Kimball ‡. This method has many advantages over the two previous methods, and it seems, therefore, useful to generalize Kimball's treatment to include the new statistics.

The basis of this new treatment is the definition of a quantity called the *range*, and its equivalence with the statistical weight. For ordinary space the dimensional range is the volume occupied by the gas. This may be analysed by taking the reciprocal of the density $\frac{1}{n}$, which is a measure of the weight or the probability of the volume state of this particle. On the *classical theory*, if there are N mass points, all of them are equally likely to be in this volume, so that N times $\frac{1}{n}$ is the weight. By similar reasoning, the range of a mass point at a particular place in the velocity space is the reciprocal of the number of particles included in unit length of the velocity space there. Likewise the momentum range per mass point is uniquely defined throughout the momentum space. The action range per unit particle is similarly defined as the product of the range per particle in the volume-space and the range per particle in the momentum space.

(2) *The Statistical Distribution Function.*

We consider, as usual, an assembly of N mass points which may be subjected to any exterior field of force, but

* Communicated by R. H. Fowler, F.R.S.

† L. W. Nordheim, Proc. Phys. Soc. A, cxix, p. 689 (1928); S. Chandrasekhar, Phys. Rev. (to appear shortly); E. Fermi, *Zeits. für Physik*, xxxvi, p. 902 (1926); L. Brillouin, *Ann. de Phys.* vii, p. 315 (1927).

‡ W. S. Kimball, Jour. Phys. Chem. xxxiii, p. 1558 (1929).

interact with each other only at very small distances. The state of such an assembly is given in the usual manner by a distribution function,

$$f(x, y, z, \xi, \eta, \zeta),$$

which gives the number of particles in every infinitesimal range $dx dy dz d\xi d\eta d\zeta$ of the given phase-space, so normalized that

$$\int f \Delta\Omega = N, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\Delta\Omega = dx dy dz d\xi d\eta d\zeta.$$

It follows, therefore, that the six-dimensional range is given by

$$\frac{1}{r} = \frac{dn}{\Delta\Omega} = f(x, y, z, \xi, \eta, \zeta), \quad . \quad . \quad . \quad . \quad (2)$$

which is the number of mass points in unit range in the volume element $\Delta\Omega$. The reciprocal of the above gives the distance there is in the phase-space between successive particles.

$$r = \frac{1}{f(x, y, z, \xi, \eta, \zeta)} = v_{i+1} - v_i. \quad . \quad . \quad . \quad (3)$$

If there are N mass points in the *classical theory*, all are equally likely to be in the range in question, independent of the number already in it, and therefore the probability that one of them will be in the specified range is N times (3). Hence the weight per particle is

$$w = \frac{N}{f(x, y, z, \xi, \eta, \zeta)}. \quad . \quad . \quad . \quad . \quad (4)$$

On the other hand, the essential feature of the Fermi-Dirac statistics is the impossibility of more than one particle occupying one and the same phase-element (according to Pauli's exclusion principle). If, therefore, the cell is already occupied, then the weight for that particular phase-element is zero. When, however, the space is not densely packed, there is correspondingly only a reduction. The simplest possible extra-factor is therefore

$$\left(1 - \frac{f}{A}\right)^*,$$

where A is the number of quantum cells in the phase-

* The weight would then reduce to zero when $A = f$, in accord with Pauli's principle.

space (for the ordinary translational motion A is, of course, equal to (m^3g/h^3)). We have in this case

$$w = \frac{\left[1 - \frac{f(x, y, z, \xi, \eta, \zeta)}{A} \right]^N}{f(x, y, z, \xi, \eta, \zeta)} \quad (5)$$

In the Einstein-Bose statistics the weight should be *increased*, and one has therefore

$$w = \frac{\left[1 + \frac{f(x, y, z, \xi, \eta, \zeta)}{A} \right]^N}{f(x, y, z, \xi, \eta, \zeta)} \quad (6)$$

With these expressions (5) and (6), instead of (4) which Kimball uses, the new statistical formulæ could be derived. Thus the weight that measured the probability that a particle will be in the i th range, corresponding to (5) and (6), is

$$w_i = \frac{\left(1 \pm \frac{f_i}{A_i} \right)^N}{f_i} \quad (7)$$

It may be necessary to distinguish between the A 's, for their masses may be different. In the case of non-degenerate systems throughout the phase-space $f/A \ll 1$, and we return to the classical theory. We have for the total weight, therefore,

$$W = \frac{\left(1 \pm \frac{f_1}{A_1} \right) \left(1 \pm \frac{f_2}{A_2} \right) \dots \left(1 \pm \frac{f_N}{A_N} \right)^{N^N}}{f_1 f_2 \dots f_N} \quad (8)$$

We will now introduce a new function g instead of f , defined by the relation

$$g = \frac{f}{1 \pm f/A} \quad (9)$$

which implies no loss of generality, since the g is a single-valued function of f . Hence

$$W = \frac{N^N}{g_1 g_2 \dots g_N} \quad (10)$$

Now we can apply the Lagrange method for conditional maxima forming the function

$$E = W + \lambda E, \quad (11)$$

where λ is arbitrary.

Taking the partial derivatives for the $3N$ independent-velocity variables,

$$\left. \begin{aligned} \frac{\partial F}{\partial \xi_r} &= -W \frac{d}{d\xi_r} \log g_r + \lambda m \xi_r, \\ \frac{\partial F}{\partial \eta_r} &= -W \frac{d}{d\eta_r} \log g_r + \lambda m \eta_r, \\ \frac{\partial F}{\partial \zeta_r} &= -W \frac{d}{d\zeta_r} \log g_r + \lambda m \zeta_r, \end{aligned} \right\} \quad . \quad . \quad . \quad (12)$$

we easily get from these relations

$$g = B' e^{c'(\xi^2 + \eta^2 + \zeta^2)}, \quad . \quad . \quad . \quad . \quad (13)$$

B' and C' being independent of the velocities. It follows, therefore, that

$$f = \frac{A}{e^{c'(\xi^2 + \eta^2 + \zeta^2)} / B \mp 1}, \quad . \quad . \quad . \quad . \quad (14)$$

i. e., the well-known Einstein or Fermi formula.

The same result can be obtained if we consider (3) and express W explicitly as a product of the successive differences of the v 's. In the classical theory (Kimball, *loc. cit.*, eq. (32) we have

$$W = N^N \prod_{i=1}^N (v_i - v_{i-1}). \quad . \quad . \quad . \quad . \quad (15)$$

On the other hand, in the quantum theory we have

$$W = N^N \prod_{i=1}^N \left(1 \pm \frac{f_i}{A_i} \right) (v_i - v_{i-1}). \quad . \quad . \quad . \quad (16)$$

If we apply, as before, the Lagrange method for conditional maxima, we get

$$\dots = \frac{\partial}{\partial v_i} \log \left(1 \pm \frac{f_i}{A_i} \right) \left(1 \pm \frac{f_{i+1}}{A_{i+1}} \right) (v_i \pm v_{i-1})(v_{i+1} \pm v_i) = 2b. \quad (17)$$

If we introduce the approximations

$$(1 \pm f_i/A_i)(1 \pm f_{i+1}/A_{i+1}) = (1 \pm f_i/A_i). \quad . \quad (18a)$$

and

$$(v_i - v_{i-1})(v_{i+1} - v_i) = (r_i)^2. \quad . \quad . \quad (18b)$$

we get the same distribution formulæ as before.

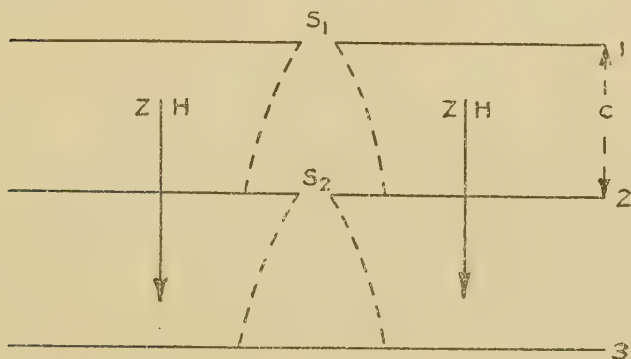
Summary.

The recently developed geometrical statistical weight theory (Kimball) has been generalized to include the quantum statistics.

LIX. *The Behaviour of Electrons in Magnetic Fields.* By V. A. BAILEY, M.A., D.Phil. (Oxon.), Associate Professor of Physics, University of Sydney*.

1. **I**N a recent communication † it has been shown how to determine the divergence of a stream of electrons which moves in a gas simultaneously under the actions of parallel electric and magnetic forces. The principle established may be illustrated by the diagram.

The stream entering at the opening S_1 diverges as it approaches the electrode 2, on account of the diffusion of the electrons, and only a certain fraction R of this stream



passes through the opening S_2 . If Z is the electric force, H the magnetic force, c the distance between the electrodes 1 and 2, k the mean energy of agitation of the electrons in terms of that of a molecule at 15°C ., and W is the mean velocity of the stream in the direction of Z , then the fraction R is a function $R(\zeta)$ of the ratio $\zeta = Z\sigma/kc$ where $\sigma = 1 + (HW/Z)^2$.

Observations on electrons in hydrogen were found to be in complete agreement with this principle, so it was applied to the determination of the velocity W in this gas and gave values which are the same as those obtained in 1921 by means of Townsend's well-known method.

* Communicated by the Author.

† See p. 560 of the present number.

Four other simple methods of applying this principle are given below. The first three are of particular interest, for, unlike the one already published, they do not require that the function $R(\zeta)$ be known. The values of W obtained by means of the different methods are all in good agreement.

2. Second Method.

The ratio R is measured with a known set of values of the electric force Z , the gas-pressure p and the spacing c ; under these conditions ζ has the value $\zeta_1 = Z/kc$. Then Z and p are diminished by the same factor n (which may have any convenient value), the magnetic force H is applied, and the ratio R is again determined; the corresponding value of ζ is $\zeta_n = Z\sigma/nkc$. The force H is adjusted to make the value R equal to that in the first set of conditions; this is equivalent to making ζ_n equal to ζ_1 . Hence $\sigma = n$, and so

$$W = \frac{Z}{H} \sqrt{n-1}. \quad . \quad . \quad . \quad . \quad (1)$$

3. Third Method.

With this the first set of conditions is the same as in the method just described, and may be represented by Z, p , and c ; therefore $\zeta_1 = Z/kc$. The second set is that represented * by Z, p, nc , and H , for which $\zeta_n = Z\sigma/knc$. The value of H is adjusted as before, which is equivalent to making ζ_n equal to ζ_1 and leads again to the relation (1).

The following table gives an actual example of its application to electrons in hydrogen:—

| Z (volts/cm.). | p (mm.). | c (cm.). | H (e.m.u.). | R . |
|------------------|------------|------------|---------------|-------|
| 20 | 4 | 2 | 0 | ·375 |
| 20 | 4 | 4 | 698 | ·375 |

Since $n = 2$ the value of W obtained by means of (1) is

$$\frac{20 \times 10^8}{698} \sqrt{2-1}, \quad i. e. 28.6 \times 10^5 \text{ cm./sec.}$$

The value obtained previously by means of Townsend's method is 25.5×10^5 .

4. Fourth Method.

The first set of conditions for this is again represented by Z, p , and c , for which $\zeta_1 = Z/kc$. The second set is represented by $Z/n, p/n, nc$, and H ; therefore $\zeta_n = Z\sigma/n^2kc$. If

* *i. e.* the only changes are an increase of the distance between the electrodes 1 and 2, and the application of the magnetic field.

H be adjusted as before, then for this value ζ_n is equal to ζ_1 . Hence $\sigma = n^2$, and so

$$W = \frac{Z}{H} \sqrt{1 - \frac{1}{n^2}}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Its application to electrons in hydrogen is shown in the following table, where $n = 2$:—

| Z (volts/cm.). | p (mm.). | c (cm.). | H (e.m.u.). | R. |
|----------------|----------|----------|-------------|------|
| 20 | 4 | 2 | 0 | ·375 |
| 10 | 2 | 4 | 626 | ·375 |

Therefore

$$W = \frac{20 \times 10^8}{626} \sqrt{1 - \frac{1}{4}} = 27 \cdot 6 \times 10^5 \text{ cm./sec.},$$

which is in agreement with the value $25 \cdot 5 \times 10^5$ referred to above.

This method is of special interest, for it can be established without neglecting any term in the complete differential equation * for the density of the electrons at a point, and because it is also suitable when negative ions are present if the instrument † with two successive chambers be used.

With this instrument the quantity $a = R(Z/kc)e^{-ac}$ is measured, where α is the probability that an electron becomes attached to a molecule per centimetre of its motion in the direction of Z. If the first set of conditions

$$Z, p, c, \text{ gives } a = Re^{-ac},$$

and the second set

$$\frac{Z}{n}, \frac{p}{n}, nc, H \text{ gives } a_{nh} = R_{nh}e^{-a_nnc},$$

then $a_{nh} = a$ when the value of H is such that $\sigma = n^2$.

For the second set R_{nh} depends on the differential equation

$$\frac{\partial^2 q}{\partial x^2} = 41 \left(\frac{Zn^2}{nkc} \right) \frac{\partial q}{\partial \zeta} - \frac{n^2}{n^2 c^2} \frac{\partial^2 q}{\partial \zeta^2},$$

which is the same as that determining R, namely,

$$\frac{\partial^2 q}{\partial x^2} = 41 \left(\frac{Z}{kc} \right) \frac{\partial q}{\partial \zeta} - \frac{1}{c^2} \frac{\partial^2 q}{\partial \zeta^2}$$

and the boundary conditions are the same too. Also

* Number (2) in the communication cited.

† V. A. Bailey and J. D. McGee, Phil. Mag. p. 1076 (Dec. 1928).

α/p depends on Z/p alone, so $\alpha_n nc = \alpha c$, and therefore $\alpha_{nh} = \alpha$. The value of H is adjusted until this condition is satisfied, and then W may be calculated by means of the formula (2).

5. Fifth Method.

Under the two sets of conditions required for the third method, let the corresponding quantities a and α_{nh} be measured. By adjustment of H , the value of α_{nh} may be made equal to $\alpha e^{-\alpha c(n-1)}$, whose value is known if that of α has already been determined. Therefore,

$$R\left(\frac{Z\sigma}{knc}\right)e^{-\alpha nc} = R\left(\frac{Z}{kc}\right)e^{-\alpha c} \times e^{-\alpha c(n-1)}.$$

$\therefore \sigma = n$, and so W may be determined by means of equation (1).

LX. *The Nature of Friction.* By Prof. P. E. SHAW,
M.A., D.Sc., University College, Nottingham*.

I.

TRIBOELECTRICITY and friction are two aspects of the same event: the rupture of the combination between atoms of solid surfaces. In friction we deal with the energetics; in triboelectricity with the electric charges caught on each of the surfaces in the act of rupture. The residual charges observed are greatest when different insulators have been in contact, but it has been shown † that charges, though smaller than these, arise when identical insulators part company; and this is also the case for identical metals provided they are parted at great speed ‡. We can express these relations in symbols. It has been established that rate of charging varies as the work done in rubbing §, so

$$\frac{dq}{dt} = a \cdot \frac{dw}{dt}$$

* Communicated by the Author.

† Proc. Phys. Soc. xxxix. p. 449 (1927).

‡ Proc. Roy. Soc. A. (1929).

§ Owen, Phil. Mag. 1909; Jones, Phil. Mag. 1925.

where

q = charge,

w = work,

a = constant, specific for the materials used.

Similarly for leakage,

$$\frac{dq'}{dt} = b \frac{dw}{dt} \cdot Q.$$

q' = leakage and re-combination,

b = leakage constant, depending on charge,

Q = accumulated charge ;

but

$$dQ = dq - dq' = (a - bQ)dw.$$

Hence

$$Q = \frac{a}{b}(1 - e^{-bw}).$$

Taking the three cases mentioned above. For unlike insulators, a is large, b small, therefore Q is large. For like insulators, a is small, b is small, Q is moderate. For like metals, a is small, b is large, Q is immeasurably small, unless by speedy separation of the surfaces b is made ineffective.

In the cases of like insulators and like metals a is small, not because the total electron flow is small, but because, for materials almost identical in nature, the flow each way across the interface is almost equal.

According to these views, friction is in all cases due to the breaking of electric attachments, and is directly proportional to the electric separation (if the flow of electrons both ways across the interface be added together) plus any work performed in *surface strain*.

We assume that when atoms meet, they invariably combine (unless they happen to be inert gases). This generalization is based on various facts :

(a) Adsorption. Here condensed vapour is strongly attached to the solid surface.

(b) The seizing of truly parallel clean surfaces when wrung together (*e.g.*, Johansson gauges). More convincing even than the seizing is the fact that after repeated wringing the surfaces are torn up, and their 'truth' ruined. In like manner many metals, initially smooth, become very rough when rubbed dry *in vacuo*.

(c) The cohesion invariably found between solid particles crystallizing from solution or emerging from fusion.

(d) Triboelectric charges. Whatever the solids used, such charges arise, as shown above, when separation occurs, and they denote combination of the surfaces before they separate. It is not implied that combination at cold contact of solids is as complete as, say, after fusion. Atoms of solid surfaces, being held by their neighbours, are not as free to form polar attachments as when in a fluid state. But there seems justification for the belief that *solid* combination does occur in kind, if not in full degree. The principle that solids invariably combine when brought into intimate contact may seem contrary to experience. For instance, such ordinary processes as hand-shaking or walking would be supremely difficult if great force were needed to break solid bonds when the hands separate, or the foot is raised from the ground. But, fortunately, the usual surface conditions in the cases cited are those described in impact (Section IV. of this paper) where dry surfaces of elastic solids are specified. If one surface were covered with an inelastic, plastic substance like pitch, cohesion on a large scale without repulsion would occur, and separation of the surfaces would become difficult. The strength of attachment of a solid for pitch, atom for atom, is small but the immense number of atoms which can combine, one substance being plastic, makes the total strength of attachment considerable.

II.

Three surface effects specially concern us in connexion with friction :—

- A. Repulsion, the direct reaction to pressure normal to the surface.
- B. Cohesion of the surfaces whilst under pressure, as displayed in sliding friction.
- C. Cohesion of the surfaces, when under tension, as in rolling friction and the rebound of impact.

The relation of B to C is obscure. We might expect the interface strength to be very different according as (in B) the normal stress between the surfaces is a pressure in some cases thousands of atmospheres ; or as (in C) it is a tension, presumably of the order of the tenacity of the material, say, a thousand atmospheres, if expressed as an inverse pressure. The strength of cohesion in each case is due to some unknown

disposition of the electric and magnetic fields of the atoms, but this disposition must be very different for compression and for tension.

Employing Hertz's equations of deformation (see Prescott's 'Applied Elasticity,' p. 632) and considering the case of a sphere touching a plane,

$$a^3 = \frac{3(1-\sigma^2) \cdot W\Re}{2\pi E}, \quad . \quad . \quad . \quad . \quad (I.)$$

$$p = \frac{3W}{2\pi a^3} \cdot (a^2 - r^2)^{1/2}, \quad . \quad . \quad . \quad (II.)$$

$$d_0 = \frac{3W}{2\pi a} \cdot \frac{1-\sigma^2}{E}; \quad . \quad . \quad . \quad . \quad (III.)$$

where

a = radius of the circular area of contact between sphere and plane,

r = any radius in this circle $< a$,

\Re = radius of the sphere,

E = Young's modulus,

σ = Poisson's ratio,

p = pressure at any point in the circle of contact,

d_0 = displacement at the centre of circle,

W = force between the sphere and plane.

By the law of friction

$$W = R = \frac{1}{\mu} T.$$

Where

R = aggregate repulsion of all atoms bearing on one another at the interface of sphere and plane.

T = aggregate cohesion of these combined atoms to resist shear.

$$\therefore R = \int_a^0 p 2\pi r dr,$$

$$T = \int_a^0 g 2\pi r dr,$$

where $p = \nu\rho$,
 $g = \nu\tau$;

where

p = pressure per unit area at any radius r in the circular area of contact as given by (II.),

g = cohesion strength per unit area at any radius,

ν = number of atoms per unit area bearing on one another across the area of contact,

ρ = repulsion per atom,

τ = cohesion per atom, to resist shear

$$\therefore W = \int_a^0 \nu \rho \cdot 2\pi r dr = \frac{1}{\mu} \int_a^0 \nu \tau 2\pi r dr, \quad \text{(IV.)}$$

clearly ν has the same values throughout on both sides of the equation, and we can apply the law of friction to the limiting case when only one atom of each surface is in contact, then

$$\rho = \frac{1}{\mu} \cdot \tau,$$

i. e., the ratio of τ to ρ is constant throughout the area of contact.

From equations (I.) and (IV.), σ , \mathfrak{H} and E being constant,

$$\int_a^0 \nu \rho 2\pi r \cdot dr \propto W \propto a^3,$$

$$\therefore \nu \rho \pi a^2 \propto a^3,$$

$$\therefore \nu \rho \propto a \propto W^{1/3}.$$

Thus, if W increases 8-fold, radius of area increases 2-fold, area 4-fold, and $\nu \rho$ 2-fold. ν and ρ increase together until the limiting pressure ρ max., sustainable by the material is reached. The solid structure then gives way at the centre of pressure. Permanent strain ensues and both the law of friction and Hertz's equations fail.

It is convenient to distinguish between permanent superficial- and permanent body-strain. All actual solid surfaces are rough compared with atomic dimensions. Even polished surfaces (whose roughness is of the order of a wave-length of light) on coming into contact meet at their outstanding protuberances. As these contact areas are small, the pressure between them is great, and this causes a flattening of the protuberances until sufficient actual contact area is developed to provide total repulsion equal to the external applied force. The superficial strain thus produced extends to a small depth, say of the order of a wave-length.

III.

Certain reactions between solid surfaces, as in impact, sliding and rolling friction, polishing, filing, and grinding are highly complex. They all bring into action on the surface atoms such large forces as to produce rupture and ionization; some of them, the last three, go further and exceed the body elastic limit. Each of the two reacting surfaces being free, has its own electrostatic and magnetic fields more complicated than in the body of the solid, where, at least in the single crystals, simplicity reigns. If further the surfaces are in contact with an atmosphere, adsorbed films and solid contamination add more factors to the equation of state. But at least we can minimize the last troubles by experimenting *in vacuo* with dry solids. We shall suppose in what follows that the reacting surfaces are dry, *i. e.*, free of even residual films.

IV.

Before dealing with friction consider a simpler effect, impact, and suppose a sphere to be approaching a plane at normal incidence. To take the sequence of events in order :

(1) The first contact is between two atoms one on each face; these combine with loss of energy and heat is developed, as in the familiar case of the surface combination known as adsorption.

(2) The two combined atoms at the interface are now at atomic distance apart and are in equilibrium; but with the onward motion of the sphere they are forced together.

Repulsion between them—due presumably to electrostatic separation and/or electromagnetic rotation—grows as the centres of the atoms approach one another, and work, most of it reversible, is performed by the oncoming sphere in building up this repulsion.

In the end, the distance between the sphere and the plane reaches its lower limit, by which time other pairs of atoms have met and undergone similar combination followed by repulsion. The sphere has now momentarily come to rest and the contact area has attained its maximum as at PPP, fig. 1. The pressure developed is maximum at O and falls to zero at the edge PPP, according to equation (II.).

Consider fig. 2 where abscissæ and ordinates stand respectively for radii of the interface and force between opposed faces.

There is an annular zone between radii a' and a in which atoms are combined, but are separated by more than atomic distance. In this zone attraction occurs across the interface, but for radii less than a' atoms are within atomic distance and repel one another. The pressure W is sustained by the algebraical sum of the total attraction A , and total repulsion R , *i. e.*, by the difference between the two shaded areas.

$$\therefore W = R - A.$$

The existence of the zone of attraction is undoubted when the surfaces are separating, and the area of contact diminishing; we assume its presence prior to this separation, though this is not essential to the argument. The annular space is negligibly small compared with the whole area πa^2 , except when this area, or the curvature of the sphere, is small, so that equations (I.) and (II.), which take no account

Fig. 1.

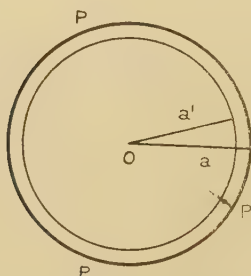
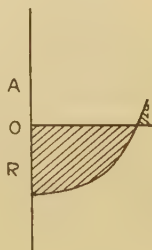


Fig. 2.



of such a zone, may for present purposes be considered valid. It is in accordance with these views that the seizing of surfaces only occurs when their curvatures are equal and opposite so that they 'fit'—flat surfaces of course being only a special case of this. In all such cases the attraction zone is relatively large, and in such an example as that quoted by G. A. Tomlinson* for lead, the attraction zone occupies the whole contact area when the pressure is negative.

(3) When the sphere rebounds from rest on the plane, the atoms in contact across the interface are torn apart, the peeling process occurring at the extreme outer edge of the annular zone, where by supposition the atoms are at more than atomic distance apart.

* Phil. Mag., June Suppl., 1929, p. 936.

The work required to break these bonds is done by the potential energy accumulated in the spring of the lattice structure.

When the rebounding sphere is nearly free of the plane and the contact area reduced to small dimensions, all the remaining pairs of atoms are in attraction. To break these remaining bonds absorbs energy from the sphere.

In the meeting and separation of the two surfaces in impact, there are losses due to various irreversible processes:

(1) During the meeting, on account of permanent displacement of atoms in the solid structure, and the combination of surface atoms; (2) during separation on account of the breaking of bonds still remaining when all the repulsion energy has been spent in the rebound.

The coefficient of restitution measured in impact experiments reveals these energy losses which, for instance, are small for steel and great for lead.

V.

Now consider sliding friction. Begin with the sphere at rest on the plane under its own weight W , and the contact area as shown in fig. 1. On applying force to draw the sphere, without rotation, over the plane, the first effect is to strain the bonds attaching the interface atoms. The bonds have a measurable elastic limit as shown experimentally by Rankin*. No rupture occurs for forces less than a critical value. When, however, sufficient tangential force T_s is applied, all the bonds formed across the interface are broken and sliding occurs. Amonton's law

$$T_s = \mu W,$$

gives the relation of the stresses to the coefficient. As sliding proceeds the bonds are continually broken and remade and, since kinetic and statical friction are equal, the total number of bonds, N , remains a statistical constant.

VI.

Next consider the case of rolling friction and imagine the sphere as before, resting on the plane under its own weight before friction commences. The law of rolling friction is

$$T_r = \lambda W,$$

where T_r is the force applied to the centre of the sphere to

* Phil. Mag., Oct. 1926.

roll it without slip (ignoring for the moment the O. Reynolds slip). λ = coefficient of rolling friction.

Imagine the force gradually applied. What first happens, as Tomlinson * showed, is that for small angular displacement of the sphere there is an elastic limit (within which the bonds are strained but hold fast). When this angle is exceeded the bonds give way not, as with sliding, over the whole area of contact, but only on the extreme periphery of the attraction zone in the wake of the rolling sphere, and corresponding new bonds form on the extreme edge in front. All the other bonds are affected but not broken as the motion commences, those in front of the centre of the interface being relaxed, and those behind strained. It is thus clear that the force required to move the sphere unit distance is less for rolling than for sliding in proportion to the bonds broken in the two cases.

We can look at it another way and consider the forces required to break a single bond (1) by rolling and, (2) by sliding. As the sphere rolls each atom as it rises from contact in the wake of the sphere traces out a cycloid.

Let the contact point move from A to O while the contact atom rises from A to P.

Let S = movement of the centre $C = OP$,

r = radius of the sphere,

θ = angle moved.

$$= \frac{S}{r}, \text{ for small angles,}$$

$$PN = r(1 - \cos \theta),$$

as θ is small,

$$\cos \theta = 1 - \frac{\theta^2}{2} = 1 - \frac{S^2}{2r^2}.$$

$$\therefore PN = \frac{S^2}{2r}.$$

Let the distance between atoms = d , and let kd = distance the bonds stretch before breaking ; if $PN = kd$,

$$s = \sqrt{2kdr}.$$

Thus the centre of the sphere moves distance $\sqrt{2kdr}$ before single rupture occurs.

Now suppose the sphere to slide, and let the distance for rupture in sliding be ld . The values of k and l may be very

* *Loc. cit.*

different; for in rolling, atoms are strained across empty space; whereas in sliding the atom of the sphere in moving from one atom on the plane never moves far from other atoms. Besides, rupture occurs, in rolling, when the atomic bonds are in *tension*, whereas they are, in sliding, *pressed* together with average forces of large amount.

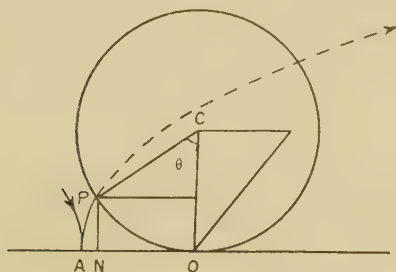
Since the coefficients λ and μ are inversely proportional to the distances required for rupture in the two cases,

$$\frac{\lambda}{\mu} = \frac{ld}{\sqrt{2kdr}} = l\sqrt{\frac{d}{2kr}}.$$

Putting $d = 2.8 \times 10^{-8}$ for steel, making $r = 1$ cm., and noting that k, l are of the order one.

$$\frac{\lambda}{\mu} \text{ is of the order } 10^{-4}.$$

Fig. 3.



Tomlinson * finds the ratio to be 5×10^{-4} for an experiment on steel. So the results by different methods are in sufficiently close agreement.

The supposition that breaking-tension in rolling equals the breaking shear-stress in sliding is conjectural. The reasoning is employed merely to compare rolling and sliding friction on the basis that both kinds are due to the breaking of solid bonds.

VII.

The laws of friction employed above can have only limited application. The law of sliding friction cannot apply when either surface has extremely large curvature as, for instance, when a sharp tool is drawn over a plane; for then flow of the material occurs in the body of the solid, and if the law

* *Loc. cit.* p. 916.

of friction were applied μ would approach infinity. Again, the law breaks down when the sum of the curvatures of the two surfaces is very small. Thus, as already mentioned, when two approximately flat surfaces bear hard on one another, and the pressure is then removed, seizure occurs and μ becomes infinite.

So far as we know, no severe experimental test of the law of sliding friction between dry solids has ever been made. Tomlinson, working on metals in the air*, has obtained a most interesting relation between the coefficient of friction and the elastic constants. In his law

$$\mu = C \cdot (v_A + v_B)^{2/3},$$

the bracket term involves compressibility and rigidity of the two solids in friction; C is a constant, varying 15–25 per cent. from its mean. Considering the uncertainty in many of the elastic constants this is good agreement, especially as readings in friction never attain high percentage constancy, and some of the irregularities in C may be due to this cause. Friction of solid surfaces is a rough-and-tumble affair depending on “catch-as-catch-can” contact of rough surfaces, and cannot be expected to have the constancy of such properties as, say, weight or rigidity.

Considering the complex relation between the pressure and area of contact of the two reacting bodies, the law of friction, as generally understood, is remarkably simple, and would seem to justify the simple conclusions reached above.

SUMMARY.

It has already been shown that the parting of solid surfaces invariably gives rise to electric separation, even when the two materials used are identical insulators or identical metals.

Thence it is assumed that what happens in all cases of solid contact is that: solid combination takes place when contact occurs: charging of both surfaces occurs when they separate. In friction, the work done is the equivalent of the work performed in total electric separation, plus any work performed in deformation of the surface structure.

The strength of attachment of two atoms (as shown in their resistance to shearing stress) and their mutual repulsion at any point of the area of contact, both vary throughout the area, but their ratio is constant. The ratio between the

* *Loc. cit.*

distances which the combined atoms separate before parting company in the two cases of sliding and rolling friction respectively, is estimated by the force required for separation in the two cases. The law of friction is limited in application; it becomes invalid for extreme curvatures as well as for extreme loading.

LXI. *A Skew Double-Slider-Crank Mechanism.* By P. CORMAC, *M.Sc., F.R.C.Sc.I., University College, Dublin* *.

THE double-slider-crank mechanism STST—the plane mechanism of four pieces, with each piece carrying the elements of a sliding and a turning pair—is met with occasionally in machinery. It derives from the quadric crank-chain by making the links a, b, c, d of infinite length, but such that a and b have a finite difference ϵ_1 , while c and d have a finite difference ϵ_2 . A special case occurs when ϵ_2 is zero. Here one of the sliding axes is parallel to the line joining the centres of the two turning pairs. A second special case occurs when ϵ_1 is made equal to ϵ_2 . Now the line joining the centres of the turning pairs always remains equally inclined to the two sliding axes. As noted by Hearson †, in this case the mechanism has a dead centre position. In the dead centre position—that is, when the sliding axes are parallel—the chain is not closed, it becoming then simply a sliding pair. It is important to note that the normal reactions on the sliders in the neighbourhood of the dead centre position may be very great.

The existence of a skew form of the double-slider-crank chain does not appear to have been previously noticed. In the skew chain the axes of the two turning pairs are parallel, the sliding axes make equal fixed angles with the turning axes, and they are equally inclined to the plane containing the turning axes. A plan of the chain is shown in the figure.

The links are numbered 1, 2, 3, 4, the sliding pairs being 14 and 23 and the turning pairs 12 and 34. If piece 1 be fixed, 2 will rotate about centre 12, sweeping out a cone of revolution, base angle α . Piece 3 maintains contact with this cone, while it may slide in the direction of the generator with which it is at the instant in contact. The locus of the

* Communicated by the Author.

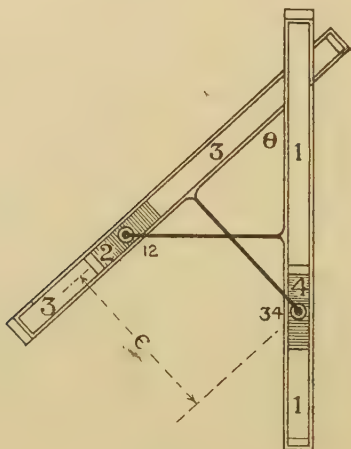
† Proc. Roy. Soc. A, clxxxvii. p. 28 (1896).

centre 34 is therefore the hyperboloid of revolution which is swept out by a generator through 34 drawn parallel to slide 3. Let slide 1 be an element of the second generation of this hyperboloid of revolution. Slide 1 will then completely constrain the path of centre 34, and will thus constrain the motion of piece 3.

The relation between the linear velocity v of the sliding pairs and the angular velocity ω of the turning pairs is

$$v = \frac{1}{2} \epsilon \omega \sec \alpha \cdot \sec^2 \frac{1}{2} \theta.$$

The skew mechanism has neither dead-centre nor change-point positions, and the normal reactions on the sliders have



always finite values. An exception, however, must be made of the particular case in which the sliding axes are perpendicular to the turning axes, the chain then becoming the special form of the plane double-slider-crank in which the sliding axes deviate by equal angles from the line through the centres of the turning pairs, a form which has been noted above.

The skew double-slider-crank chain derives from Bennett's* skew parallelogram chain by passing two alternate vertices of the skew isogram to infinity. It may thus be classified as a special case of the skew isogram.

As the four pieces are similarly placed in the chain, the four possible inversions result in the same mechanism.

* Proc. Lond. Math. Soc. xiii. p. 151 (1914).

LXII. *On the Scattering and Diffraction of Cathode-Rays.*

By PAUL WHITE, B.A. (Cantab.), Carnegie Teaching Fellow in the University of Aberdeen*.

1. *Introduction.*

WHEN a narrow pencil of electrons falls upon a thin sheet of amorphous material, its individual members suffer various deflexions by the atoms through which they pass, and the pencil as a whole is scattered. If it then falls normally on a photographic plate placed a short distance away from the scattering material, the blackening produced on development will be a maximum in the centre where the whole pencil would have fallen if no matter had been in its path, and with increasing distance from the centre will fall off symmetrically on all sides.

Recently, however, G. P. Thomson and Reid† have shown that if the film through which the electrons pass is microcrystalline, there may appear superimposed on this distribution of electrons other electrons, scattered in an alternative manner, their angles of deviation having, not the continuous range of values present in the previous case, but a number of discrete values. These are recorded on the photographic plate as rings concentric with the central spot produced by the former set of electrons.

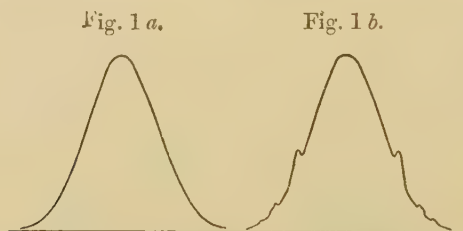
We can describe the effect quantitatively by plotting against the distance r , measured from the centre of symmetry of the photograph, the number of electrons per unit area falling on the plate at that distance r and thus obtaining what may be called an electron-distribution curve. It has long been known that when the scattering material is amorphous, the curve has the general form given by Gauss's Error Law (fig. 1*a*) for suitable incident velocities of the electrons and sufficiently great film-thicknesses. No experiments have hitherto been made to determine the curve when the scattering material is microcrystalline, but it is clear that the general form in this case will be that shown in fig. 1*b*, in which each pair of symmetrically-disposed small maxima corresponds to one ring on the photographic plate, that is, to one discrete value of the angle of deviation.

* Communicated by Prof. G. P. Thomson.

† G. P. Thomson and A. Reid, 'Nature,' exix. p. 890 (1927); G. P. Thomson, Proc. Roy. Soc. cxvii. p. 600 (1927).

The former type of scattering has been subjected to numerous investigations, and the results can be fairly completely described in terms of classical mechanics*. It is only possible to give an account of the phenomenon discovered by Thomson and Reid in terms of wave-mechanics. In the one case the electron is regarded as a charged particle deflected by the electrostatic attraction of an atomic nucleus or of several atomic nuclei successively; in the other it is considered as a train of de Broglie waves diffracted by the atoms and hence reflected by suitable net-planes in the minute crystals of the scattering material as are the X-rays in a Debye-Scherrer powder experiment.

While the radii of the rings have been critically compared with the wave-length relations suggested by



General form of electron distribution curve for amorphous and micro-crystalline materials respectively: strictly diagrammatic.

wave-mechanics, the subject of intensities has been hitherto practically untouched. In particular no data have previously been given for the relative numbers of electrons occurring in the central spot and in the rings.

The aim of the present work was to determine electron-distribution curves experimentally, and hence to deduce the relative numbers of electrons falling in the central spot, in one of the rings or in the continuous background. Since the visibility of rings depends on their sharpness of resolution and high intensity relative to the background, a knowledge of the factors governing these quantities will enable us to arrange the most favourable conditions for observing rings in difficult cases.

* W. Bothe, *Zs. f. Phys.* iv. p. 300, v. p. 63 (1921). Compare Geiger and Scheel's 'Handbuch der Physik,' xxiv. (article by Bothe), pp. 15-18.

2. *Experimental Method.*

A photographic method was used, and the number of electrons per unit area falling in the neighbourhood of any point was deduced from the optical density of the image there. The mode of obtaining the photographs was exactly that used by Thomson and Reid (*loc. cit.*). A very fine pencil of cathode rays emerged from a discharge-tube through a cylindrical channel in the anode 6 cm. long and 0.0115 cm. in radius. The high-tension supply to the tube was derived from an induction coil with mercury-interrupter, rectifying valve, and Leyden jars, and was of the order of 30 kilovolts. G. P. Thomson has shown that electron-beams so obtained are very nearly homogeneous and have a velocity very nearly corresponding to the whole fall of potential across the tube as measured by a pair of spark-balls in parallel with it.

The pencil of cathode-rays was scattered by a film of gold of the order of 10^{-6} cm. thick, placed close to the exit-aperture of the channel in the anode, and fell normally upon a photographic plate placed 32.7 cm. from the gold.

Paget process plates were used and developed in hydroquinone until the optical density was judged suitable for photometry.

Exposures varied from a few seconds to several minutes. The camera was fitted with a device for moving the plate rapidly (under gravity) without letting the vacuum down; by this means two exposures were made immediately after one another on each plate under rigorously identical conditions, except that their durations, which were measured, were in the ratio of about one to three. By this device it is possible to convert densities of the images to terms of relative numbers of electrons incident per unit area, in spite of the fact that very little is known of the photographic characteristics of plates for electrons of these velocities. (See below, pp. 645, 646.)

The optical densities of the images were measured with a microphotometer of the Lindemann type at a series of points lying on a line through the centre of the figure. The microphotometer was by the Cambridge Instrument Company.

3. *Thickness of Gold Films.*

The films were prepared by sputtering gold upon a skin of cellulose acetate and dissolving the latter away with

acetone in the manner recommended by Jolyot and developed by Thomson * for this type of work.

Their thicknesses (order of 10^{-6} cm.) were found in the following way from their opacities.

It can easily be shown that when a parallel beam of light of wave-length λ cm. in air falls normally upon a thin plane-parallel sheet of absorbing material of thickness t cm. and complex refractive index, $n+ik$, the ratio of the transmitted to the incident *intensity* is equal to

$$\frac{16 \overline{(n^2 + k^2)}}{(n+1)^2 + k^2} \cdot \frac{\exp\left(-\frac{4\pi kt}{\lambda}\right)}{1 - 2r \cos(2a + \phi) \exp\left(-\frac{4\pi kt}{\lambda}\right) + r^2 \exp\left(-\frac{8\pi kt}{\lambda}\right)},$$

where r is the reflexion-coefficient of the substance in bulk

(for *intensities*), and is equal to $\frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$,

$$\tan \alpha = \frac{2k}{n^2 + k^2 - 1}$$

$$\text{and} \quad \phi = \frac{2\pi}{\lambda} \cdot 2nt.$$

All these constants have been measured by Hagen and Rubens† for thin films of gold for a large range of wave-lengths, and we can accordingly deduce the thickness if the opacity is known. In order to do so rigorously we should need to use monochromatic light; but this is inconvenient experimentally, and by a fortunate accident turns out to be unnecessary in the case of gold.

For a considerable range of wave-lengths to be admissible in the light used, it is sufficient that the opacity should be sensibly the same throughout the range; for otherwise a system of weighting the wave-lengths would be necessary in working out the results, and in practice would be quite impossible to perform. Now, the photometer used for finding the opacities of the gold films (as also of the plates) acts by means of a potassium photo-cell. Accordingly the effective wave-lengths lie between the photo-electric threshold of potassium and the limit of transparency of the glass of the lenses etc.; the largest part of the response of the instrument must be caused by radiation

* Proc. Roy. Soc. cxxv. p. 352 (1929).

† Hagen and Rubens, *Verh. d. Deut. Phys. Ges.* iv. p. 55 (1902).

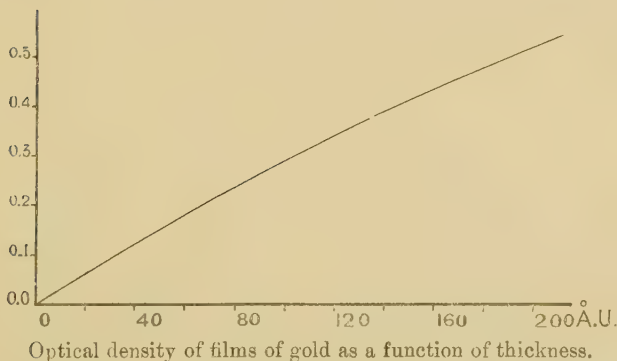
well within these wave-length limits, say, between 3750 Å.U. and 5000 Å.U. By calculating from Hagen and Rubens's data the opacity of a gold film 100 Å.U. thick for a number of wave-lengths, it can be shown that there is only a small variation in the range in question. We are accordingly able to employ white light with the same simplicity as monochromatic light, and to calculate opacities from the data for a mean wave-length.

In fig. 2 the optical density so found is plotted against thickness of gold.

The following values were assumed :—

$$\begin{aligned}\lambda &= 4500 \text{ Å.U.}, & n &= 1.53, \\ r &= 0.34, & k &= 1.73\end{aligned}$$

Fig. 2.



A small error enters on account of the convergence of the beam falling on the film in this photometer. It would be very tedious to evaluate a correction for this accurately, but a rough estimate shows that it is only of the order of 1 or 2 per cent., which is less than the macroscopic variation in thickness in a single film.

4. *Measurement of Plates.*

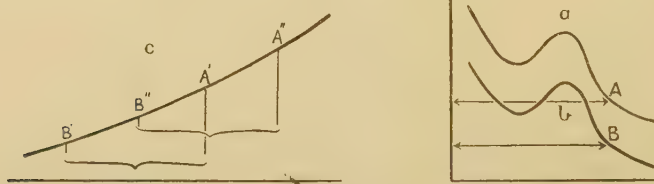
By means of the microphotometer mentioned above the distribution of optical density along a line through the centre of each image was measured, and these readings were plotted as in fig. 3, *a* and *b*.

In order to convert these readings to terms of numbers of electrons incident per unit area, it is necessary to correct for the characteristics of the photographic plate. Unfortunately, very little is known with certainty about the

behaviour of plates for electrons of these velocities. The following procedure, however, enables us to determine the characteristic curve directly and individually for each plate, and for exactly the electron-speed and conditions of development used in each case. It assumes only that the Reciprocity Law holds for electrons of these velocities; that is, that the time of exposure necessary to produce a given blackening of the plate is inversely proportional to the intensity of the electron-beam. This is known to be so from the work of Bothe*.

This method, which may be called the method of duplicate exposures, is capable of wide application where the photographic characteristics are unknown but the Reciprocity Law holds. Two exposures whose durations were in a known ratio were made on each plate, and both images were measured on the photometer and optical

Fig. 3.



Construction of characteristic curve *c* (density against log of exposure) from a pair of photometer curves *a* and *b*.

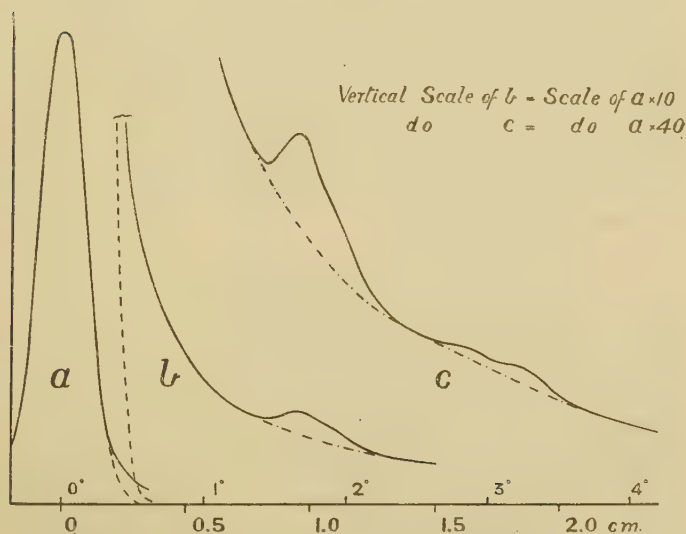
density plotted against position as in fig. 3, *a* and *b*, where the ratio of times is one to three. Now, if two points A, B are found, one on each curve, at equal distances from their respective central ordinates, they correspond to points on the plate where the intensities of electron-illumination were the same, since the conditions are the same for the two exposures, but the durations of illumination were in the ratio 3 : 1. The ordinates A, B must therefore be the ordinates (optical densities) of two points A', B' on a characteristic curve (fig. 3, *c*) whose distance apart in abscissa (logarithm of total exposure) is $\log_{10} 3$. Since the zero of abscissa has no absolute significance in fig. 3, *c*, we can plot B' at once and A' from it. In the same way we can obtain an indefinite number of pairs of points (A'', B'') whose ordinates and the difference of whose abscissæ

* W. Bothe *Zs. f. Phys.* viii. p. 243 (1922) : xiii. p. 106 (1923).

are known. It is necessary to choose the absolute value of their abscissæ so that one smooth curve can be passed through all the points. This is easily secured after one or two trials, and actually the result depends hardly at all on the judgment of the draughtsman, as an unskilful choice of the point A'' is revealed at once by the awkward position which results for B''.

When the characteristic curve has been drawn, the curves of fig. 3, *a* and *b*, can at once be replotted in terms of relative intensities of electron-illumination (*cf.* fig. 4, which is a composite curve, discussed in next paragraph).

Fig. 4.



Experimental curve of electron distribution.

Except for a multiplicative constant, the curves for the two exposures should give the same result, and in practice the discrepancy is less than the error of the individual points.

It would be possible to obtain a characteristic curve directly by making a number of exposures of known durations and measuring the density of the central spot in each case. The present method, however, enables the exposures to be completed rapidly, and so reduces the danger of failure due to small changes in the hardness of the discharge-tube. It also avoids the necessity for measuring

accurately many small intervals of time, and leads to the correction of each point on fig. 3 by data derived from itself and similarly disposed points, and hence avoids uncertainty due to local exhaustion of the developer at dense points.

5. *The Curves of Electron-Intensity.*

The results obtained after correction for the photographic characteristics of the plates in the manner described above (§ 4) are plotted in fig. 4, in which ordinates are numbers of electrons falling per unit area, and abscissæ either distances along the plate (r) or angles of deviation by the film. Owing to the large range of ordinates involved, it was not possible to obtain the whole curve from one pair of exposures, and it was necessary to compile it from the results of a series of plates taken with the same electron-velocity and the same gold film (not merely with another film of the same measured thickness). The sections into which fig. 4 is divided are chosen for convenience in drawing, and do not correspond in any way to the parts measured on single plates.

Each curve consists of a central maximum and subsidiary maxima in symmetrically-disposed pairs, each pair corresponding to one ring on the plate: for the sake of clarity, only the maxima on one side of the centre are shown in the figure. The central portion agrees closely with the form given by Gauss's Error Function, $e^{-\frac{x^2}{a^2}}$, within a distance of about 2 mm. on each side. Further out, the experimental ordinates are greater than the Gaussian. The dashed line of fig. 4 is a prolongation of the best-fitting Gaussian curve. The chain-dotted lines are interpolations beneath the subsidiary maxima, and divide the part of the area of the curve attributed to rings (which is also very closely of Gaussian form, where resolved) from that attributed to background.

Plates were obtained corresponding to energies between 20,000 volts and 48,000 volts and thicknesses of gold between 110×10^{-8} cm. and 250×10^{-8} cm. The rings were not prominent for the lower voltages, and the slowest electrons for which it was profitable to photometer their traces were of 30,000 volts.

It may be said at once that the general scale of intensities of the rings is governed, in so far as it depends upon

the film, not only by the mean thickness, but also by some further unidentified factor or factors. Two films of the same optical density give the same ratio between the intensities of various rings (for electrons of the same speed), but, in general, different ratios between the intensities of central spot, rings, and background*. As the nature of these other factors defining the properties of any individual film is obscure, no profitable investigation of the dependence upon film-thickness of the proportion of electrons appearing in the rings could be made; further work on this point is proceeding. Moreover, the data are only strictly comparable among themselves when drawn from a series of plates obtained with one and the same film. The films are eventually punctured by the electron beam and rendered useless. If this occurs before a whole series of satisfactory plates has been taken, the work already done on the particular film is rendered of little value except to confirm the general trend of results given by a more permanent film. Most of the data quoted in this paper have been corroborated in a general way by such fragmentary results.

6. Compensation of Instrumental Effects.

The curves obtained after correcting for the non-linearity of the photographic law certainly give the relative number of electrons per unit area falling in the neighbourhood of any point; but before any useful data of general significance can be drawn from them, it is necessary to compensate them for several effects which give rise to spurious broadening of the central spot and loss of resolution of the rings. Even in the absence of a gold film the trace obtained on the plate is not a geometrical point, but has a finite size, due to :—

(a) Finite breadth and cross-firing of the initial beam of electrons;

(b) their mutual repulsion while passing down the camera;

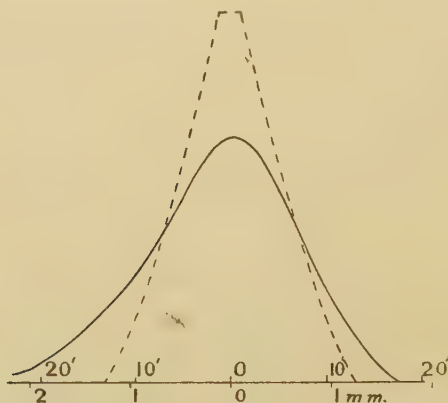
(c) scattering by residual gas in the camera;

(d) scattering and irradiation in the sensitized layer of the plate.

* Cf. Rupp, *Ann. der Phys.* i. p. 773 (1929).

All these agencies affect equally well the trace obtained in the presence of a gold film, and it is necessary to estimate their total effect and to correct the results embodied in fig. 4 for it as follows. The total effect can be found experimentally by exposing a plate without inserting a gold film. In fig. 5 is shown the curve so obtained (smooth curve) with electrons of 30 kilovolts, and also the curve calculated for the effect (α) only (broken line). It appears that this geometrical effect is capable of explaining nearly all the finite size of the observed trace, and as it is independent of the voltage of the electrons, it is possible to

Fig. 5.



Finite breadth of unscattered beam. Full line: experimental. Broken line: geometrical effect only. The slight asymmetry in the experimental curve is probably due to a minute curvature of the channel in the anode.

consider as constant the size of the trace in the absence of gold, at least for the moderate ranges of voltage involved.

The problem of compensating for this parasitic broadening of the image, that is, of deducing from the curves of figs. 4 and 5 a curve corresponding to an ideally narrow initial beam, is dealt with in an Appendix. The solution will clearly be a curve in which the individual features are sharper than in fig. 4, but in which the relative areas of the various parts are unchanged. In the Appendix it is shown that it is legitimate to consider the several sections independently with the following results (the experimental curve of fig. 5 being taken to be Gaussian):—

(1) The central maximum remains of Gaussian form, its square-parameter being reduced from its experimental value (measured from fig. 4) by the square-parameter of the spurious broadening curve (measured from fig. 5, smooth curve).

(2) The maxima corresponding to rings also remain Gaussian, and are reduced in breadth in the same way (but retain their distance from the centre to a first approximation).

(3) The background to these subsidiary maxima, since its form cannot be represented analytically in any simple way, could only be treated numerically and at great labour. However, in the remoter parts of the field its ordinate only varies slightly in a distance equal to the whole breadth of the curve of fig. 5, and here the parasitic effects can simply be neglected.

7. Results. *The Central Maximum.*

The discussion of results falls naturally into three parts: the form of the central maximum with the general background; the form of the rings; and the relation between the magnitudes of the different parts of the curve.

Since the central maximum was always nearly Gaussian in form:

$$y = y_0 \exp\left(-\frac{x^2}{a^2}\right),$$

the results can be conveniently tabulated by giving values of the parameter a , which serves as a measure of the breadth of the peak and is referred to here as the "half-breadth." The quantity a^2 is the "square-parameter" of the last paragraph. The half-breadth was estimated in two ways from the curves, a_1 being calculated from the measured area and height of the hump in the curve ($\text{Area} \div \text{Height} = \sqrt{\pi} \cdot a_1$), and a_2 being obtained by halving the distance between the points at which the curve fell to $\frac{1}{e}$ of its maximum height.

The close agreement between a_1 and a_2 serves to confirm that the form of the curve is Gaussian.

In Table I. the experimental half-breadths are given for those sets of conditions for which a full range of plates

was obtained. The column headed A gives the values of the half-breadths obtained by correcting for the finite size of the initial beam; we may call this quantity the "true half-breadth." The column headed θ gives the latter expressed as angle of deflexion by the film.

The quantity K tabulated in the last column is defined as

$$K = \frac{A \text{ (in mm.)} \times \text{Energy (in electron-K.V.)}}{\text{Film-thickness (in \AA.U.)}}$$

This quantity is calculated for the purpose of comparison with the classical theory of scattering. It is not unreasonable to suppose in the first place that the electrons which appear in the central maximum have been scattered in the ordinary way by collision with the gold atoms of the film,

TABLE I.
Half-breadth of Central Maximum.

| Voltage. | Film thickness. | a_1 . | a_2 . | A. | θ . | K. |
|----------|-----------------|----------|----------|----------|------------|------|
| 30 K.V. | 0 | 1.00 mm. | 1.04 mm. | 0 | 0 | — |
| 30 „ | 140 A.U. | 1.31 „ | 1.29 „ | 0.80 mm. | 0°140 | 2.03 |
| 30 „ | 250 „ | 1.59 „ | 1.57 „ | 1.18 „ | 0°207 | 2.24 |
| 45 „ | 140 „ | 1.15 „ | 1.16 „ | 0.51 „ | 0°090 | 1.94 |

and to test this we compare K with the value predicted by theory. The calculated half-breadth depends somewhat on the radial distribution assumed for the electrons about the gold nucleus. Bothe (*loc. cit.*) has given a formula founded on a uniform volume distribution of electrons through a sphere, which leads to a value 470 for K, as against 2 from the present work. We should expect such an assumption to lead to prediction of a somewhat excessive amount of scattering, as we now know that the electron-density in an atom increases rapidly as the nucleus is approached, and the screening of the nuclear field is therefore actually greater than given by uniform distribution. The change in K produced by such a modification of the theory (*e.g.* by assuming Thomas's data * for the atomic field) is however not large; indeed, the theory without modification agrees very satisfactorily with the only other measures of multiple scattering of

* L. H. Thomas, Proc. Camb. Phil. Soc. xxiii. p. 542 (1927).

electrons available—those of Crowther* for β -rays of 600 K.V. We are therefore led to the conclusion that the electrons forming the central spot have not been scattered in accordance with classical theory. The half-breadth calculated for electrons of 30 K.V. and films of 10^{-6} cm. is of the order of 10 cm. as against 1 mm. here observed.

Two explanations of the presence of these unexpectedly lightly-scattered electrons are possible. It is not unlikely that the effect is in part due to submicroscopic non-uniformity of the film. Minute areas may be exceptionally thin, and there may actually be holes through which electrons can pass almost unscattered. It is however possible that the central maximum constitutes an interference maximum of zero order. This view is further examined below (§ 9). In practice both effects probably occur, but it is impossible to distinguish electrons which appear in the central spot after having passed through holes from those which passed through the full thickness but remained unscattered. The films were examined carefully under a high magnification, and only such as showed uniformity of opacity and complete absence of holes were used. Since, however, their mean thickness corresponded to only about 40 atom layers (80 if face-centring atoms are counted separately), it is very probable that gaps are present which, if they are of width of the same order as the thickness of the film, will not be visible under the microscope. The method of preparation by sputtering would certainly lead us to expect considerable irregularities; moreover, in the case of rolled films ($\frac{1}{50}$ mm. thick), which are presumably much more compact than sputtered films, Evans and Bannister† have been led to assume the presence of cracks emerging to the surface and having a width “a few times the diameter of an iodine molecule,” *i. e.* say 10–20 Å.U.

Although it has been shown that some electrons escape the scattering process, others must also occur which have been scattered to the full extent required by the classical theory. These we should expect to be distributed according to a Gaussian law with half-breadth of the order of 10 cm. (20°). Unfortunately, the angles subtended by the plate at the gold film in the present apparatus are too

* J. A. Crowther, Proc. Roy. Soc. lxxxiv. p. 226 (1910).

† U. R. Evans and L. C. Bannister, Proc. Roy. Soc. cxxv. p. 370 (1929).

small to observe any but the inner portions of such a distribution, *i. e.* up to about 3 cm. (6°) from the centre. Over a region of this size the incidence of fully-scattered electrons should thus be practically uniform, and we cannot distinguish the blackening of the plate caused by these electrons from the continuous background (if any) formed by parasitic causes such as X-rays generated in the film. In order to form an estimate of the way in which the continuous background varies at greater distances from the centre, and thus to gain some idea of what fraction of its intensity is due to extraneous causes, exposures were made with a bar-magnet fixed near the camera in a plane midway between the film and the plate. The field was sufficient to deflect the central spot several centimetres. There appeared to be a residual effect of appreciable magnitude, but very much smaller than the effect due to electrons (order of one-twentieth of the background intensity near the centre). The electronic effect varied with the distance from the centre in a way somewhat different from that required by the function $\exp\left(-\frac{x^2}{a^2}\right)$, falling more rapidly in the inner parts and less rapidly in the outer parts. This is in accordance with what is to be expected when the film is not of uniform thickness (a number of component Gaussian curves of different breadth giving an aggregate curve of this general form) and when multiple scattering gives place to plural scattering.

8. *The Rings.*

Maxima corresponding to reflexions from the following planes were dealt with :

(111), (200), (220), (311), (222), (331), (420),

but of these the fourth could not be resolved from the fifth, nor the sixth from the seventh. In each case the rings appear resolved to the eye, which is peculiarly sensitive to *gradients* of blackening (especially when arranged in a recognizable geometrical form), but the photometric traces were hopelessly entangled. The first and second also overlapped considerably, but by replotting on a large scale it was possible to apportion the area of the curve between them tolerably accurately.

In Table II. are given the results from a very complete series of plates which were measured in detail. All data

referring to film-thickness 140 \AA.U. were obtained from the same film, and are thus comparable *inter se*. The areas under the maxima (not including background), the heights of the maxima from the background level, and the magnitudes of the background under each ring are given in arbitrary units, the latter two being to the same

TABLE II.
Dimensions of Rings.

| Plane. | Area. | Height. | Back-ground. | N. | a_1 . | a_2 . |
|--|----------------------|---------|--------------|-------|----------|----------|
| 30,000 volts; thickness 250 \AA.U. | | | | | | |
| 111 | 11.9 | 7.2 | 10.1 | 23.3 | 0.93 mm. | 0.84 mm. |
| 200 | 4.1 | 2.9 | 9.4 | 8.2 | 0.80 „ | 0.75 „ |
| 220 | 3.7 | 2.4 | 7.4 | 10.5 | 0.91 „ | 0.87 „ |
| 311 } 222 } | 4.7 | 2.4 | 6.6 | 16.0 | | |
| 331 } 420 } | 1.7 | 0.95 | 5.2 | 7.4 | | |
| 45,000 volts; thickness 140 \AA.U. | | | | | | |
| 111 | 4.4 | 2.9 | 7.0 | 7.6 | 0.86 | 0.90 |
| 200 | 1.4 | 1.0 | 5.9 | 2.8 | 0.78 | 0.80 |
| 220 | 1.5 | 0.8 | 4.2 | 4.2 | 1.06 | 1.02 |
| 311 } 222 } | 3.0? | 1.0 | 3.4 | 10.2? | | |
| 331 } 420 } | 1.25 | 0.5 | 2.0 | 5.4 | | |
| 30,000 volts; thickness 140 \AA.U. | | | | | | |
| 111 | 7.2 | 3.8 | 11.0 | 12.5 | 1.07 | 1.05 |
| 200 | 2.1 | 1.5 | 9.2 | 4.2 | 0.80 | 0.79 |
| 220 | 0.8 | 0.45 | 5.9 | 2.3 | 1.10 | 1.00 |
| 311 } 222 } | 1.45 | 0.75 | 4.7 | 4.9 | | |
| 331 } 420 } | This ring very weak. | | | | | |

scale, and the first to this scale multiplied by millimetres. The quantities a_1 , a_2 are, as before, the parameters of the Gaussian curve to which the profile of each ring approximates and serve, as before, as a measure of the breadth of the trace; N is the relative number of particles falling into each ring, and is proportional to the product of the area under the maximum and the radius of the ring in question.

The most striking feature of this table is the approximate constancy of the half-breadth of the rings. The extreme variation in a is only 35 per cent. for a simultaneous change of 50 per cent. in the energy of the rays and 80 per cent. in the thickness of the foils. A very curious result appears, however, when the mean value of a (0.90 mm.) is compared with the half-breadth of the central spots given in Table I. Not only do all the central maxima have greater half-breadths than any of the rings, but also the unscattered beam shows a greater value than the majority of the rings; that is, these rings are narrower than the minimum breadth admissible on geometrical grounds. It might therefore be supposed that the half-breadths of the subsidiary maxima are being systematically underestimated. The only way in which this can occur seems to be that the background has been interpolated too high everywhere. The displacement of the chain-dotted lines in fig. 4, necessary to give the narrowest ring the minimum geometrical breadth only is, however, about 10 per cent. of the background-ordinate, and must be applied everywhere if the background is to be represented by a smooth curve. This implies that no rings whatever are resolved, and gives a very awkward and improbable form to the profile of each. The anomalous sharpness of these traces appears, therefore, to be an objective phenomenon. We may conclude that if it were not masked by the finite breadth of the initial beam, the resolving power of the gold film would be very high.

9. *General Magnitudes. Discussion.*

In order to find the total (relative) number of electrons falling within given limits of distance from the centre, the number of electrons per unit area at each distance must be multiplied by that distance and the product integrated. Fig. 6 is obtained from fig. 4 by multiplying each ordinate by the corresponding abscissa, and therefore areas in the figure so formed are proportional to total numbers of electrons. The broken curves have the same significance as before. The areas of the various portions of the figure are given in arbitrary units in Table III. for the case of film-thickness 140×10^{-8} cm. and electrons of 30 kilovolts.

The entry for "background within 2 cm. of centre" refers to a much larger area on the plate than any entry

above it, and it is accordingly the only one on which the spurious contribution due to X-rays etc. has any appreciable effect. Although the magnitude of the necessary correction is not known exactly, it is certainly not large (*cf.* end of §7).

The radius 2 cm. within which the background is measured has no real significance. This figure is simply

Fig. 6.

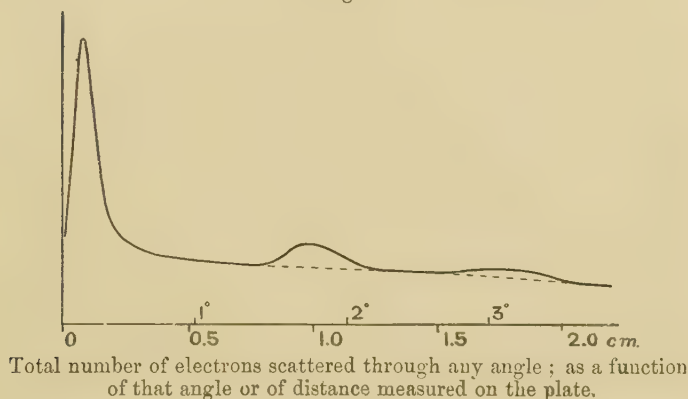


TABLE III.

| Region. | Relative number of electrons. |
|--|-------------------------------|
| Central maximum | 60 |
| Ring (111) | 7.1 |
| „ (200) | 2.4 |
| „ (220) | 1.3 |
| „ (311+222) | 2.7 |
| Background within 2 cm. of centre | 180 |
| Total background | Order of 300 |

quoted as an indication of the magnitude of the effect involved, because the whole background cannot be accurately measured on the present apparatus. The only data available for the intensity further out are those obtained by shifting the electron pattern to the side of the plate by means of a magnet (§7). This process certainly

introduces errors, but serves to give us the order of magnitude of the total effect (order of 300 units).

We have shown that the films are not uniform in thickness. For this reason it is impossible to obtain all the information we hoped for from these data, and the experiment must be regarded as a preliminary one. If we knew that all electrons passed through the same thickness of gold, we could work out from the intensities of rings and background the relative proportion of elastic and inelastic scattering. Unfortunately, when the films are not uniform, the rings are mainly due to those electrons that have passed through the thinner parts of the film, while the background is derived from all parts. We cannot draw any conclusions from the relative intensities until we know more about the variations of the film.

It might at first appear that no rings ought to be expected at all, since the conditions for multiple scattering are satisfied in the region in question for films several times thinner than the average thickness of those used in these experiments. On the other hand, even when multiple scattering occurs, there will be a finite probability that a particle will emerge having made only one serious collision. When this collision is elastic such particles appear as rings. It would be very difficult to calculate the chance that a particle should experience one collision violent enough to deflect it to form part of a ring system, and no other sufficiently serious to throw it out again; but a rough estimate based on Lennard-Jones and Woods's* data for the distribution of electron-density in a lattice of heavy atoms indicates that the probability is very small indeed. On the other hand, the fact that rings are experimentally observed shows that it cannot be negligible in the conditions occurring in these experiments. The electrons forming rings must have passed through the thickness of gold, and cannot have been reflected from planes of atoms forming the walls of cracks in the films, since the rings have those radii which are calculated for the case in which refraction of the train of de Broglie waves on entering the metal is not considered, and the angle of incidence must therefore have been considerable.

If the conditions are such that an appreciable number of electrons make one serious collision only (deflexion of 1°

* J. E. Lennard-Jones and H. J. Woods, Proc. Roy. Soc. cxx. p. 727 (1928).

or more, say), and that one, moreover, elastic, there must be also an appreciable number which have made no serious collision at all. The wave-trains corresponding to electrons which have not been scattered, or which have been elastically scattered through very small angles, will be in phase, and will therefore interfere constructively to form part of the central spot. For slightly larger angles of scattering the phase agreement will be imperfect, and the intensity accordingly less. The central spot will therefore have a finite breadth which corresponds to the finite breadth of the spectrum of zero order in diffraction theory.

It would be interesting to know what fraction of the total number of incident electrons thus penetrates practically unscattered. But the present results will give us only an approximate estimate, as we do not know with certainty the total magnitude of background, nor to what extent the incident beam passes through holes in the film. In order to form an accurate estimate of this ratio, an apparatus is now under construction in which the angle subtended by the photographic plate at the gold film is very much larger than in the present apparatus, and in which the film can be swung out of the path of the beam without letting down the vacuum. It will, therefore, be possible in successive exposures to measure the unscattered beam and the whole of the scattered beam, and thus to obtain this ratio accurately.

Summary.

The angular distribution of electrons of about 30 K.V., after scattering by sputtered films of gold about 200 A.U. thick, has been found by measuring with a photometer photographs of the type obtained by Thomson and Reid. A method is described for calculating from the photographic densities the number of electrons falling upon unit area, even when the photographic characteristics are unknown. The relative intensities and profile of the rings, central spot, and general background have been measured. The profile of the rings is inexplicably sharp. The central spot is probably due partly to electrons which have passed through holes in the film, and partly to electrons which have passed through the thickness of the film but have remained unscattered although the conditions for multiple scattering are in this case satisfied. The general background is due to electrons which are scattered either inelastically or more than once.

I am glad to have this opportunity of expressing my gratitude to Prof. G. P. Thomson for his very stimulating advice and discussion during the progress of this work.

Appendix.

If $y=g(r)$ represents the number of electrons falling per unit area at a distance r from the centre of symmetry of the figure, when the instrumental causes of finite breadth alone act (*cf.* fig. 5), $y=f(r)$ the required distribution corresponding to infinitely narrow initial beam, and $y=F(r)$ the resultant effect which is experimentally determined (fig. 4), it is easy to see that the three functions are related by the equation :

$$F(R) = \int_0^\infty \int_0^{2\pi} f(\sqrt{r^2 + R^2 - 2Rr \cos \theta}) \cdot g(r) \cdot r d\theta dr.$$

Since this is linear in F and f , the subdivision of the area under $F(r)$ into sections for separate consideration, as carried out in § 5, is justified.

Moreover, if f and g are Gaussian functions each symmetrical about the origin and of parameters a , b respectively, we have :

$$\begin{aligned} F(R) &= \int_0^\infty \int_0^{2\pi} \exp\left(-\frac{r^2 + R^2 - 2Rr \cos \theta}{a^2}\right) \exp\left(-\frac{r^2}{b^2}\right) r d\theta dr \\ &= \int_0^\infty \exp\left(-\frac{r^2 + R^2}{a^2} - \frac{r^2}{b^2}\right) \cdot \sum_{t=0}^\infty \frac{2\pi}{(t!)^2} \left(\frac{R^2 r^2}{a^4}\right)^t r dr \\ &= \frac{\pi a^2 b^2}{a^2 + b^2} \exp\left(-\frac{R^2}{a^2 + b^2}\right), \end{aligned}$$

and the curve of fig. 6 is Gaussian with parameter $\sqrt{a^2 + b^2}$. This is the case of section (1) of § 5.

The integral corresponding to section (2) of § 5 runs :

$$\int_0^\infty \int_0^{2\pi} \exp\left(-\frac{r^2 + R^2 - 2Rr \cos \theta}{a^2} - \frac{(r-p)^2}{b^2}\right) r d\theta dr,$$

where p is the radius of the ring in question. This cannot be evaluated in finite terms. If, however, the radius p is large compared with the breadths a and b , as is always the case in practice, we may neglect the curvature and write the integral :

$$\int_0^\infty \int_0^\infty \exp\left(-\frac{(x-x')^2}{a^2} - \frac{(y-y')^2}{a^2}\right) \exp\left(-\frac{(x-p)^2}{b^2}\right) dx dy,$$

which equals

$$\frac{\pi a^2 b}{\sqrt{a^2 + b^2}} \exp\left(-\frac{(p-x')^2}{a^2 + b^2}\right),$$

again of Gaussian form with parameter $\sqrt{a^2 + b^2}$.

If f is a constant, the double integral is no longer a function of R , and F is a constant also.

LXIII. *Hydrogen and Helium Lines as Standards of Wave-length.* By W. G. PENNEY, A.R.C.S.*

IN connexion with the use of the lines of the Lyman series of hydrogen as standards of wave-length in the far ultra-violet, the question was raised by Professor A. Fowler as to the correct theoretical expression for their wave-number. From the theory it is known that these lines actually are doublets, but the resolving power of spectroscopic apparatus in the region of 1000 Å.U. is at present insufficient to reveal this fine structure, which is further obscured by the comparative breadth of the lines themselves. In the absence of any detailed information regarding this breadth, one may consider the measurements to refer to the centre of gravity of the two components in each line, and the wave-number of this may be computed since the theory furnishes us with the wave-numbers and the relative intensities of the individual components. The same remark applies to the lines of the Balmer series in spectrograms where they are unresolved, and to the lines in the spectrum of He^+ which correspond to the Lyman and Balmer lines.

On the following page are given diagrams showing the origin of the various component lines in the two series. Disregarding at first the electron spin, the level with principal quantum number n consists of n component levels distinguished by the azimuthal quantum number l , which takes the values $0, 1, \dots (n-1)$. Taking the spin into account, each level l splits up into two component levels with total quantum number $j = l \pm \frac{1}{2}$, excepting the level $l=0$, which remains single and has the value $j = \frac{1}{2}$. These new levels, however, coincide again in pairs, which are bracketed together in the diagrams, excepting the level with the largest value of j . The new levels have energy values given, according to Dirac, Darwin, and Gordon†, by the original

* Communicated by Prof. S. Chapman, F.R.S.

† P. A. M. Dirac, Proc. Roy. Soc. A, cxvii. p. 610 (1928); C. G. Darwin, Proc. Roy. Soc. A, cxviii. p. 654 (1928); W. Gordon, *Zett. f. Phys.* xlviii. p. 11 (1928).

fine structure formula of Sommerfeld, referring to an atom with nuclear charge Z and a single electron,

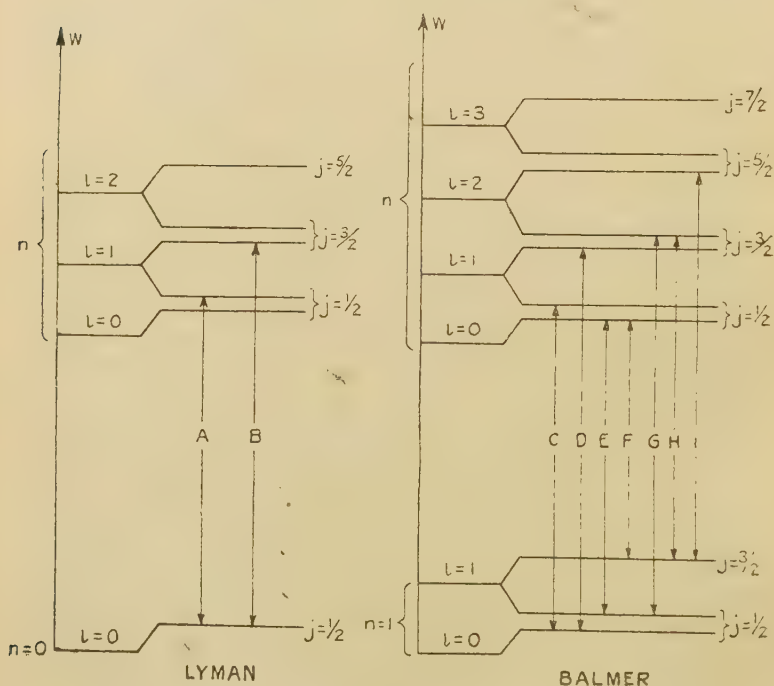
$$W = -\frac{Z^2 R c h}{n^2} \left[1 + \frac{Z^2 \alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right], \quad (1)$$

in which higher powers of the small quantity

$$\alpha^2 = 5.31 \times 10^{-5}$$

have been neglected, while R denotes the Rydberg constant, c the velocity of light, and h Planck's constant. The component lines are subject to the selection rules

$$\Delta l = \pm 1, \quad \Delta j = 0 \text{ or } \pm 1$$



The lines of the Lyman series are thus seen to consist of two, and those of the Balmer series of five, components, since C coincides in wave-number with E , and D with G . The relative intensities are, according to the theory*, given by the following proportions:

$$A : B = 1 : 2 \quad (2)$$

* M. V. Sugiura, *Journ. de Phys.* viii, p. 3 (1927); *Scient. Papers of the Inst. of Phys. and Chem. Res. Tokyo*, No. 193 (1929); W. Gordon, *Ann. d. Phys.* ii, p. 1031 (1927).

for the components of the Lyman lines, and

$$(C + E) : (D + G) : F : H : I = \left[\frac{4}{n^2} + \frac{1}{3(n^2 - 1)} \right] : \left[\frac{8}{n^2} + \frac{32}{3(n^2 - 4)} \right] : \frac{2}{3(n^2 - 1)} : \frac{32}{15(n^2 - 4)} : \frac{96}{5(n^2 - 4)} \quad (3)$$

for the components of the Balmer lines.

The wave-number of the centre of gravity of the various lines may then be calculated by means of the equation

$$\nu = \frac{\sum g_i \nu_i}{\sum g_i}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the ν_i are the wave-numbers of the components and the g_i proportional to their intensities. With the help of equations (1) to (4) there results for the wave-number of the Lyman lines

$$\nu = Z^2 R \left(1 - \frac{1}{n^2} \right) + Z^4 R \alpha^2 \left(\frac{1}{4} - \frac{2}{3n^3} + \frac{3}{4n^4} \right), \quad . \quad (5)$$

and for the Balmer lines

$$\nu = Z^2 R \left(\frac{1}{4} - \frac{1}{n^2} \right) + Z^4 R \alpha^2 \left(\frac{137n^4 - 384n^2 + 240}{192(5n^2 - 4)(3n^2 - 4)} - \frac{109n^4 - 284n^2 + 160}{15n^3(5n^2 - 4)(3n^2 - 4)} + \frac{3}{4n^4} \right). \quad (6)$$

The value of the Rydberg constant R has been very accurately determined, both for H and He^+ , by Houston* with the help of interferometric measurements of the individual components of the first two lines in the Balmer, and the first line of the Fowler series respectively. He finds

$$R_H = 109677.76 \pm 0.02,$$

$$R_{He} = 109722.40 \pm 0.02$$

with his own estimate of error. Using equations (5) and (6) and the values given for R and α^2 , the frequencies of the centre of gravity of the first three lines in the Lyman series and the first six lines in the Balmer series of H , as well as those of the corresponding lines in the spectrum of He^+ , have been computed. The results are compiled in the Tables.

The calculated values of the centre of gravity of the lines considered here agree within the experimental error with the empirical ones determined by Curtis and Lyman† for

* W. V. Houston, *Phys. Rev.* xxx. p. 608 (1927).

† See A. Fowler, 'Report on Series in Line Spectra.'

H and He⁺, but excepting the Balmer lines of H these latter are not accurate enough to show if the correction of the unresolved lines for their fine structure improves the agreement or not. Work is now in progress in Professor Fowler's laboratory with the object of increasing the precision of wave-length determinations in the ultra-violet, which will necessitate taking the correction into account for these other lines as well.

Hydrogen.

| LYMAN. | | BALMER. | | |
|-------------|-----------------|-------------|-----------------|-----------------|
| ν_{vac} | λ_{vac} | ν_{vac} | λ_{vac} | λ_{air} |
| 82259.77 | 121.5664 | 18238.282 | 4340.346 | 4340.755 |
| 97492.71 | 1025.718 | 20564.819 | 4362.673 | 4361.319 |
| 102824.81 | 972.383 | 28382.384 | 4341.675 | 4340.489 |
| | | 24679.067 | 4102.855 | 4101.791 |
| | | 23451.386 | 3971.457 | 3970.068 |
| | | 20746.786 | 3889.148 | 3889.048 |

Helium†.

| ν_{vac} | λ_{vac} | ν_{vac} | λ_{vac} |
|-------------|-----------------|-------------|-----------------|
| 329187.1 | 305.779 | 60960.24 | 1640.413 |
| 390146.0 | 256.314 | 82295.62 | 1215.131 |
| 411481.6 | 243.024 | 92170.83 | 1081.941 |
| | | 97335.22 | 1025.271 |
| | | 100769.75 | 992.361 |
| | | 102869.07 | 972.109 |

I should like to express my thanks to Dr. R. de L. Kronig for many helpful suggestions.

Imperial College of Science,
South Kensington, S.W. 7.
January 30, 1930.

Corractor's Note.—There appeared in 'Nature,' cxxv, p. 235 (1930), measurements by Ealen and Edlén on the lines of Li⁺⁺, Be⁺⁺⁺ corresponding to the Balmer and Lyman series of H, but again these are not accurate enough to show if the correction for fine structure improves the agreement or not.

LXIV. *The Space-Group of the Alkaline Sulphates.* By Professor A. OGG, *Physics Department, University of Cape Town* *.

MY conclusion † that the space-group of the alkaline sulphates is V_h16 has been confirmed ‡ by W. Taylor and T. Boyer. Since, however, F. P. Goeder assigns § some of these sulphates to the space-group V_h13 it is necessary to reconsider the evidence. Dr. A. E. H. Tutton in a recent paper || considers that the balance of the evidence is in favour of V_h16 . It can easily be shown that in order to satisfy the symmetry of the group V_h13 , the conditions of the X-ray spacings of the group V_h13 are that

- (i.) planes of the type (hkl) have their spacings halved if $(h+k)$ is odd ;
- (ii.) planes of the type (hko) have their spacings halved if $(h+k)$ is odd ;
- (iii.) all other planes have normal spacings.

Since the selection of the axes relative to the elements of symmetry is arbitrary, we can say from the above conditions that two of the pinakoid spacings must be halved, while one must be normal. According to the experimental evidence, all the pinakoid spacings are halved. The space-group V_h13 is therefore untenable. The space-group V_h16 is the only group which satisfies the spacings of the X-ray reflexions.

Dr. Tutton has compared ¶ the dimensions of the crystal unit obtained by Ogg and Hopwood in the first investigations ** with those †† of Taylor and Boyer and finds a maximum difference of half a per cent. It is interesting to compare the experimental data with the dimensions calculated from fundamental physical constants and Tutton's values of the densities and axial ratios.

The volume of the unit is given by

$$V = abc = \frac{nMe}{\rho cF},$$

* Communicated by the Author.

† Proc. Roy. Soc. S. Africa, July 1927 ('Nature,' cxx. p. 408, 1927); Phil. Mag. v. p. 354 (1928).

‡ Mem. and Proc. Manchester Lit. and Phil. Soc. lxxii. p. 125 (1928).

§ Proc. Nat. Acad. of Sci. of U.S.A. xiii. p. 793 (1927) and xiv. p. 766 (1928).

|| Phil. Mag. viii. no. 49, p. 195 (1929).

¶ Loc. cit.

** Phil. Mag. xxxii. p. 518 (1916).

†† Loc. cit.

where abc are the sides of the unit, n the number of molecules per crystal unit = 4, M the molecular weight, e the charge on an electron = $(4.774 \pm 0.005)10^{-10}$ e.s.u., ρ the density, c the velocity of light = $(2.99796 \pm 0.00004)10^{10}$ cm./sec., F the Faraday = (9648.9 ± 0.7) e.m.u.

A comparison of the calculated dimensions with the published experimental results shows that the results of W. Taylor and T. Boyer are in closest agreement with the calculated values, the maximum difference being 0.2 per cent.

The following table shows how close the agreement is for the two salts investigated by them :—

TABLE I.

| Crystal. | Calculated dimensions. | | Observed dimensions. |
|--------------------|---------------------------|--|--|
| | Volume 10^{-24} c.c. | Axes 10^{-8} cm. | (Taylor and Boyer) Axes 10^{-8} cm. |
| K_2SO_4 | 431.52 | $\begin{cases} a & 5.757 \\ b & 10.056 \\ c & 7.457 \end{cases}$ | |
| Rb_2SO_4 | 487.50 | $\begin{cases} a & 5.984 \\ b & 10.458 \\ c & 7.827 \end{cases}$ | |
| $(NH_4)_2SO_4$... | 492.26 | $\begin{cases} a & 5.976 \\ b & 10.608 \\ c & 7.764 \end{cases}$ | 5.98 10.62 7.78 |
| Cs_2SO_4 | 562.94 | $\begin{cases} a & 6.248 \\ b & 10.937 \\ c & 8.237 \end{cases}$ | 6.24 10.92 8.22 |

TABLE II.

| Distances between Atomic Centres. | | |
|-----------------------------------|--------------------------|-----------------------------------|
| | From sulphates (Ogg). | Sum of atomic radii (Pauling). |
| K—O | 2.71 A. | 2.73 A. |
| Rb—O | 2.89 | 2.88 |
| Cs—O | 3.10 | 3.09 |

Another point of interest is that the shortest distance * between the centres of the metals and oxygen in the structure given by me is in agreement with the sum of the atomic radii calculated by Pauling from the conception of wave mechanics.

University of Cape Town,
October 1929.

Note by Dr. A. E. H. TUTTON, F.R.S., Cambridge.

The further evidence now presented by Prof. Ogg, from his latest measurements, renders it clear that the space-group of the alkali sulphates is undoubtedly $V_h 16$. Moreover, in his paper read on July 25th at the 1929 Meeting of the British Association at Cape Town, when the writer of this note was present, Prof. Ogg gave the following as his latest and most accurate X-ray measurements of the absolute lengths in Ångström units (10^{-8} cm.) of the orthorhombic unit-cell-edges.

| | <i>a.</i> | <i>b.</i> | <i>c.</i> |
|--------------------|-----------|-----------|-----------|
| K_2SO_4 | 5.76 | 10.05 | 7.46 |
| Rb_2SO_4 | 5.97 | 10.43 | 7.81 |
| $(NH_4)_2SO_4$... | 5.97 | 10.60 | 7.76 |
| Cs_2SO_4 | 6.24 | 10.93 | 8.23 |

The values for all four salts are remarkably close to the calculated values given in his present Table I.; and the values for the ammonium and caesium salts are equally close to, practically identical with, those of Taylor and Boyer. The greatest difference anywhere is only 0.02 (0.2 per cent.). Also it may be pointed out that the distances between the atomic centres of the nearest metallic and oxygen atoms given in his Table II. are further confirmed by the very similar values which have been published by Wasastjerna from optical data, and by V. M. Goldschmidt for co-ordination number [6].

These highly satisfactory later results confirm and yet more fully emphasise the conclusions published by the writer in his communication to this Magazine in August 1929 on the "Significance of X-Ray Analysis of Alkali Sulphates" †.

* Phil. Mag. v. p. 354 (1928).

† Phil. Mag. viii. p. 195 (1929).

LXV. *Critical Stresses for Tubular Struts.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

REGARDING Professor Andrew Robertson's letter in your February issue concerning my paper on "Critical Stresses for Tubular Struts," I should like to say that no reference to practical applications is made in the paper because it is solely concerned with the interpretation of a mathematical equation.

I should also like to correct a few errors which appear on p. 1065 of the paper. Near the top of the page "The minimum value of this" should read "The minimum value of p ." Immediately following equation (11), "where $A = \frac{1}{3} \frac{t^2}{a^2} \frac{m^2}{m^2 - 1}$ " is omitted; and lower down the page, "For instance if $m = 2$ " should read "For instance if $k = 2$."

The College of Technology,
Manchester.
February 12, 1930.

Yours faithfully,
H. CARRINGTON.

LXVI. *Notices respecting New Books*

Source Books in the History of the Sciences. A Source Book in Mathematics. By DAVID EUGENE SMITH, Ph.D., LL.D., Professor Emeritus in Teachers College, Columbia University, New York City. (London: McGraw-Hill Publishing Co. Price 25s. net.)

THE publishers of this series of Source Books aim at presenting the most significant passages from the work of the leading scientists of the last three or four centuries. With such a wealth of material accumulating a demand for selected sources necessarily arises. This series, indeed, breaks new ground, and puts together in an accessible form carefully selected material which in due course will cover the leading Physical and Biological Sciences.

The general editor, Professor G. D. Walcott, of Brooklyn, N. Y., began to organize the Advisory Board in 1924, and to Professor D. E. Smith was allotted the task of carrying out the general idea in the field of Mathematics.

The material in his volume covers the $4\frac{1}{2}$ centuries closing with the year 1900. Over such a wide field the task of selection has necessarily presented many difficulties.

The field of Number starts at the logical beginning of the subject, and extends to even such a modern development as Nomography.

The field of Algebra is interpreted to cover Equations Symbolism, and Series, the early method of solving the cubic and biquadratic equations and numerical equations of higher degree and so on.

To the person interested in statistics the special section devoted to Probability is most welcome.

The field of Geometry ranges from the contributions from such 16th century writers as Fermat, Desargues, Pascal and Descartes, to a few of those who, in the 19th century, revived the study of the subject and developed various forms of modern geometry.

The fields of Calculus, Function Theory, Quaternions, and the rest of mathematics presented a formidable task, but some attention has been paid to each domain.

The student of the history of mathematics will welcome this book with avidity. Its standard of scholarship is high, and there is evidence that the difficult decisions which have at many points confronted the organizers of this work have been made with wisdom and the greatest of care.

The Great Mathematicians. By H. W. TURNBULL, M.A., Regius Professor of Mathematics in the University of St. Andrews. (London: Methuen & Co., Ltd. Price 3s. 6d. net. 1929.)

THIS little book will be sure of a warm welcome from all those who are interested not only in the subject matter of Mathematics, but also in its history. The inevitable drawback that mathematical study is saturated with technicalities from beginning to end, often means in practice that the student has little time or opportunity to study its history.

In this little book Professor Turnbull has been specially concerned with revealing something of the spirit of Mathematics, without unduly burdening the reader with intricate symbolism.

In view of the new significance of Mathematics as the basis of all sciences, such a task is well worth performing. The student not only of Mathematics, but also of Physics, Chemistry, and Bio-Chemistry, and, indeed, of any of the precise sciences will find the information it contains valuable and stimulating.

Professor Turnbull should be congratulated on his success in showing how a mathematician thinks, and how his imagination, as well as his reason, leads him to new aspects of the truth.

Logic for Use. By F. C. S. SCHILLER, Fellow of Corpus Christi College, Oxford, Fellow of the British Academy. (London: Bell & Sons, Ltd., 1929. Price 16s. net.)

IN this book Dr. Schiller outlines the new logic which systematically scraps the cardinal notions of the traditional logic—formal validity, absolute truth, logical necessity, absolute certainty, and all-inclusiveness—and replaces them by real truth, progressive knowledge, purposive connexion, probability, and relevant selection.

How far he has been successful in this task will be an open question. That there is room for such a work is undeniable.

The book is, of course, a sequel to the author's 'Formal Logic.' Most of it was actually delivered in a course of special lectures in the University of California in 1929. It has, in fact, been

planned as much for the student of the sciences as for those to whom the study of logic has been a traditional occupation.

The author is of the opinion that the study of modern logic, while still in its infancy, will be capable, possibly in the course of a few centuries, of developing into a body of knowledge.

With the author's hope and belief that this subject ought to be progressive like the sciences, one cannot but have sympathy, but it would be difficult to see in the present work a suitable foundation for such a body of knowledge.

The work is marred by the author's habit of tilting at windmills, which cannot but repulse the student who, even if he has not suffered from the alleged drawback of an Oxford education, will be more concerned to try to find a logic useful to him in his scientific work than to study the inter-relations of the author's views, at once iconoclastic and vague, and the traditional idea of logic, which, as all the world knows, belongs not to the laboratory, but to the study thick with the dust of the ages.

As a part of a general education in the art of thinking, the student with sufficient time and the necessary drive may be recommended to give this book a cursory reading.

Handbuch der Experimental Physik. Herausgegeben von W. WIEN und F. HARMS. Band 8, erster teil, geb. R.M. 65. Band 9, erster teil, geb. R.M. 44.60. (Akademische Verlagsgesellschaft, m.b.H., Leipzig.)

IN the first of these volumes—Energie und Wärmehalt—the editor, Prof. A. Eucken, has given a comprehensive survey of the experimental researches in this special branch of physics; so far as it is possible to keep pace with the rapid progress which has been made in recent years, this book provides a very complete and up-to-date summary of results, especially the experimental methods of thermometry and calorimetry and the experimental determination of specific heats of solids, liquids, and gases. A large amount of information is brought together on the measurement of heats of solution, dilution and combustion. Although the experimental aspect of the subject has been emphasized, the theoretical investigations of Debye and others have not been omitted.

The four sections of the second volume are devoted to the subjects of the production and measurement of high and low temperatures, the liquefaction of gases, the conduction and radiation of heat. Prof. Wien, the chief editor of this encyclopædic handbook, and Dr. Müller were responsible for the section on radiation. Soon after the completion of this work Prof. Wien died, and this volume may be regarded as a worthy memorial of one of the greatest research workers in physical science. His contributions to the theory of black body radiation, as set out in his two laws, the displacement law and the energy distribution formula, were of capital importance, and showed the way to the complete solution of this problem. A beautiful portrait of

Prof. Wien forms the frontispiece of this volume. Extensive indexes of authors and subjects and numerous references to original papers are given in both volumes: in printing, binding, and illustration a very high standard has been reached. The editors and publishers deserve the highest commendation for their enterprise in providing these valuable books of reference for workers in this branch of physics.

Leçons de Mécanique Rationnelle, Tome deuxième. Par FRANÇOIS BOUNY. (Paris: Librairie Scientifique. Albert Blanchard, 3 et 3 bis, Place de la Sorbonne. 1929. Prix 90 frs.)

THE first volume of this work was published five years ago and provided an introductory course to the study of statics, dynamics, potential and the theory of linear vectorial functions. The application of these functions to the problems of moments of inertia and the dynamics of solid bodies generally is made in the second volume, which is devoted to the study of the dynamics of a point and of systems. The author gives a detailed account of vibrations and resonance, especially the vibrations of strings and rods, the torsional vibrations of shafts, etc., phenomena which are of increasing importance in both mechanical and physical science. The theory of vibratory movements is completed by the application of the Lagrange equations to the study of small movements about a position of stable and unstable equilibrium. The notion of the gyroscopic couple is introduced, based upon a paper contributed by the author to *L'Enseignement mathématique* about fifteen years ago. A clear and interesting treatment is also given of topics which are indispensable for the effective study of recent developments in mathematical physics. The importance of laboratory practice and manipulation in the study of theoretical mechanics are recognized by the attention given to the experimental measurement of moments of inertia, of vibrations, damped and undamped, and gyroscopic couples. A valuable feature of the book is the inclusion of numerous exercises given at the end of the chapters, some of them with fully worked-out solutions.

LXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 328.]

November 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

‘The Upper Estuarine Series of Northamptonshire and Northern Oxfordshire.’ By Beeby Thompson, F.G.S., F.C.S.

In Northamptonshire, between the Lincolnshire Limestone and the Great Oolite Limestone in north-eastern parts of the county,

and between the Northampton Sand (or the Lower Estuarine Beds) and the Great Oolite Limestone in all other parts of the county, occurs a series of variable beds, largely variegated clays containing abundance of vegetable matter of probably freshwater origin, interspersed with brackish-water beds and with distinctly marine beds. To this aggregate J. W. Judd, in 1867, gave the name 'Upper Estuarine Series', which he then thought represented the Stonesfield Slate or Lower Zone of the Great Oolite of the more south-westerly parts of England, Oxfordshire particularly.

An addition to Judd's general description was made by the Author in 1909 ('Water-Supply of Bedfordshire & Northamptonshire') in the introduction of 'Upper Estuarine Limestone', commonly a water-bearing bed in the midst of the series, and now generally recognized. This bed actually divided the series into three parts, a division retained in this paper, but to which is added much additional information, palæontological and other, about each part.

In Northern Oxfordshire, between certain Inferior Oolite Limestones or White Sands (the time-equivalents of the Lincolnshire Limestone?), or Ferruginous Sands (the equivalents of the Variable Beds of the Northampton Sand or even of the Ironstone Series) below, and the Great Oolite Limestone above, occurs a series of beds which in various parts physically, and in others palæontologically, agree, as does the complete set in sequential position, with the Upper Estuarine Series of Northamptonshire. It is an important object of Part I of this paper to show how the Northamptonshire and Oxfordshire sections on this geological horizon may be more definitely correlated.

A type-section of the Upper Estuarine Beds of Northamptonshire is given with extended explanation. A comparison of Northamptonshire and Northern Oxfordshire sequences, as given by the Author, M. Odling, and E. Walford, is made, in an attempt to show the approximate equivalence of the Upper Estuarine Limestone of Northamptonshire with the Chipping Norton Series of Oxfordshire, making allowances for much more variability in character of the series in Oxfordshire than in Northamptonshire, and particularly, in places, the extension of marine beds into the lower part.

Part II includes a large number of illustrative sections for Northamptonshire, in which it is shown how the extended classification of beds can be used for identifying unconformities due to earth-movements developed at different times.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]